

**BARRIER COMPOSITION**

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**Abstract of JP2002128847**

**PROBLEM TO BE SOLVED:** To obtain a barrier composition to reduce or eliminate poisoning or contamination of a photoresist layer or an antireflective coating layer caused by a dielectric layer. **SOLUTION:** This barrier composition contains one or more crosslinkable polymers, one or more acid catalysts, one or more crosslinking agents and one or more solvents, where at least one of the crosslinkable polymers and the crosslinking agents has one or more acid parts. The acid parts mean herein one or more acid groups contained in the crosslinkable polymers, crosslinking agents or both of them.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The constituent with which it is a barrier constituent containing the polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, and one or more solvents, and at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts.

[Claim 2] The constituent according to claim 1 with which the polymer which can construct a bridge has one or more aromatic series hydroxyl compounds as a polymerization unit.

[Claim 3] The constituent according to claim 1 with which the polymer which can construct a bridge contains one or more aromatic aldehyde condensates.

[Claim 4] The constituent according to claim 1 with which an acid part does not contain a blocking radical selectively at least.

[Claim 5] The constituent according to claim 1 with which the polymer which can construct a bridge contains one or more aromatic aldehyde condensates and one or more acrylate (meta) polymers.

[Claim 6] How to be an approach of offering a barrier layer on a dielectric base, be a constituent containing the polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, and one or more solvents, and include the process which arranges the polymer which can construct a bridge, and the constituent with which at least one of the cross linking agents has one or more acid parts on the front face of a dielectric base.

[Claim 7] The approach according to claim 6 the polymer which can construct a bridge contains one or more aromatic series hydroxyl compounds as a polymerization unit.

[Claim 8] The approach according to claim 6 the polymer which can construct a bridge contains one or more aromatic aldehyde condensates.

[Claim 9] The approach according to claim 6 an acid part does not contain a blocking radical selectively at least.

[Claim 10] The approach according to claim 6 the polymer which can construct a bridge contains one or more aromatic aldehyde condensates and one or more acrylate (meta) polymers.

[Claim 11] The approach according to claim 6 by which a dielectric base is applied by a physical vapor deposition or chemical vacuum deposition.

[Claim 12] The approach according to claim 6 a dielectric base is an inorganic substance.

[Claim 13] The approach according to claim 6 a dielectric base contains silicon.

[Claim 14] The device which it is the device which has a dielectric layer and the barrier layer arranged on it, and this barrier layer has the polymer in which one or more bridge formation is possible as a polymerization unit, and one or more cross linking agents, and contains the polymer which can construct a bridge, and one or more polymers in which at least one of the cross linking agents has one or more acid parts, and over which the bridge was constructed.

[Claim 15] The device according to claim 14 which furthermore has a photoresist layer.

[Claim 16] The device according to claim 14 which includes further the antireflection coating arranged between a barrier layer and a photoresist layer.

[Claim 17] The device according to claim 14 with which a barrier layer has the thickness from about 200Å to about 1.5 microns.

[Claim 18] The device according to claim 14 with which a dielectric layer is applied by a physical vapor deposition or chemical vacuum deposition.

[Claim 19] The device according to claim 14 whose dielectric layer is an inorganic substance.

[Claim 20] The device according to claim 14 with which a dielectric layer contains silicon.

[Claim 21] How to be a method including arranging a barrier layer between a dielectric layer and a photoresist layer of decreasing the contamination of a photoresist layer, and for this barrier layer have the polymer in which one or more bridge formation is possible as a polymerization unit, and one or more cross linking agents, and contain the polymer which can construct a bridge, and one or more polymers in which at least one of the cross linking agents has one or more acid parts and over which the bridge was constructed.

[Claim 22] The approach according to claim 21 the polymer which can construct a bridge contains one or more aromatic series hydroxyl compounds as a polymerization unit.

[Claim 23] The approach according to claim 21 the polymer which can construct a bridge contains one or more aromatic aldehyde condensates.

[Claim 24] The approach according to claim 21 an acid part does not contain a blocking radical selectively at least.

[Claim 25] The approach according to claim 21 the polymer which can construct a bridge contains one or more aromatic aldehyde condensates and one or more acrylate (meta) polymers.

[Claim 26] The approach according to claim 21 a dielectric base is an inorganic substance.

[Claim 27] The approach according to claim 21 a dielectric base contains silicon.

[Claim 28] The approach according to claim 21 a barrier layer has the thickness from about 200Å to about 1.5 microns.

[Claim 29] a) The process which offers a dielectric layer on a base, the polymer which can construct a bridge beyond b1, The barrier constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts including one or more acid catalysts, one or more cross linking agents, and one or more solvents the process arranged on the front face of a dielectric layer, and c -- the manufacture approach of an electron device which heats a base to sufficient temperature to harden a barrier constituent selectively at least, and includes the process which forms a barrier layer.

[Claim 30] a) The process which offers a dielectric layer on a base, the polymer which can construct a bridge beyond b1, The barrier constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts including one or more acid catalysts, one or more cross linking agents, and one or more solvents A base is heated to sufficient temperature to harden a barrier constituent selectively at least. the process arranged on the front face of a dielectric layer, and c -- The manufacture approach including the process which forms a barrier layer, the process which arranges antireflection coating on the front face of d barrier layer, and the process which arranges a photoresist layer on the front face of e antireflection coating of an electron device.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001] Generally this invention relates to manufacture of an electron device. This invention relates to the photoresist and antireflection coating which are used in manufacture of an electron device more at a detail.

[0002] In manufacture of electron devices, such as a printed circuit board or a semi-conductor, the layer of many matter, such as a photoresist or antireflection coating, is applied on a base. A photoresist is a photographic sensitive film used for imprinting an image to a base. The coating layer of a photoresist is formed on a base and a photoresist layer is exposed by the activity radiation source through a photo mask (reticle (reticle)) next. A photo mask has other penetrable fields to an impermeable field and an impermeable activity radiation to an activity radiation. If it exposes with an activity radiation, the chemical changeover induced by the light of photoresist coating will take place, and the pattern of a photo mask will be imprinted by the wrap photoresist in a base. After exposure, a photoresist is developed, a relief image is acquired, and, thereby, alternative processing of a base is attained.

[0003] A photoresist can be either a positive type or a negative mold. or [ carrying out the polymerization of the part for these coating layers exposed with an activity radiation about almost all the negative-molds photoresist in the reaction between the optical activity compound (photoactivecompound) of a photoresist constituent, and a polymerization nature reagent ] -- or a bridge is constructed. Therefore, the exposed coating part cannot melt easily into a developer rather than a part for an unexposed part. Although the part exposed about the positive type photoresist becomes easy to melt by the inside of a developer, the amount of unexposed part cannot continue melting into a developer comparatively easily. It is well-known in this industry, and a photoresist constituent is Deforest and Photoresist. Materials and Processes, McGraw Hill Book Company, New York, Chapter 2, 1975 and Moreau, Semiconductor Lithography, Principles, Practices and Materials, Plenum Press, New York, Chapter 2, and Chapter 4 (the part all indicate a photoresist constituent, its manufacturing method, and a usage to be is referred to as a part of this invention).

[0004] The main applications of a photoresist are the activities in semi-conductor manufacture, and the object is forming beer, a trench, or structure like those combination in a dielectric layer. It is important in order that suitable photoresist processing may attain this object. Although powerful interdependence is among various photoresist processing processes, it is thought that exposure is one of the more important processes which acquires a high-resolution photoresist image.

[0005] It sets in such a process and an echo of the activity radiation between exposure of a photoresist and "poise NINGU (poisoning)" of the photoresist by the dielectric layer are harmful because of formation of detailed structure. For example, an echo of the activity radiation from the lower layer of a photoresist restrains the resolution of the image patternized in the photoresist layer in many cases. An echo of the radiation from a base / photoresist interface can fluctuate the radiation intensity in a photoresist during exposure, consequently the line width of face of a photoresist becomes an ununiformity at the time of development. Further, radiations can be scattered about all over a photoresist field without the intention to expose, and fluctuation of line width of face produces them from a base /

photoresist interface also by this. Dispersion and the amount of echoes change with locations typically, consequently line width of face becomes an ununiformity further.

[0006] An echo of an activity radiation serves as a cause of the phenomenon further known for this industry as "standing wave effectiveness (standing wave effect)." In order to abolish the effectiveness of the chromatic aberration in the lens of an aligner, in a photoresist projection technique, monochrome or semi- monochromatic radiation is usually used. However, when using monochrome or semi- monochromatic radiation for photoresist exposure for an echo of the radiation in a photoresist / base interface, especially interference and destructive interference that suit in slight strength are remarkable. In such a case, the reflected light interferes with incident light and forms a standing wave in a photoresist. Since the thin layer of a photoresist with insufficient (underexposed) exposure is formed by the pole dot of a standing wave with the big amplitude in the case of a high reflexivity base field, a problem gets worse. The layer with insufficient exposure can bar the development of a perfect photoresist, and the problem of an edge AKUI tee (edge acuity) produces it in a photoresist profile. Since the total amount of the radiation required in order to expose this will increase if the amount of photoresists increases, generally the time amount required in order to expose a photoresist is the increasing function of the thickness of a photoresist. However, in the thickness direction of a photoresist, the higher harmonic (harmonic component) which changes between maximum and the minimum value continuously is included between exposure for the standing wave effectiveness. When the thickness of a photoresist is uneven, a problem becomes still more serious and line width of face is changed.

[0007] By the orientation latest [ to a high density semiconductor device ], there is a motion which shortens wavelength of the exposure light source in the industrial world like deep ultra-violet (DUV) light (wavelength is 300nm or less), KrF excimer laser light (248nm), ArF excimer laser light (193nm), an electron ray, and soft X ray. Generally by using for image-ization of photoresist coating the light which shortened wavelength, the echo from a resist up front face and a lower base front face increases. Thus, the activity of shorter wavelength worsens the problem of the echo from a base front face.

[0008] The further approach used in order to reduce the problem of the reflected radiation was using the absorption-of-radiation layer called the top antireflection coating or TARC arranged on the absorption-of-radiation layer called the bottom product antireflection coating or BARC between a base front face and a photoresist coating layer, or the front face of photoresist coating. For example, it is reference [ No. / [the part which indicates all the acid-resisting (antihalation) constituents in these reference and the activity of those is referred to as a part of this invention] / the PCT application WO 90/No. 03598, the Europe patent application 0639941A No. 1 and U.S. Pat. No. 4910122, No. 4370405, and / 4362809 ]. Generally such BARC and a TARC layer are also indicated by reference as an acid-resisting layer or an acid-resisting constituent. Typically, such an acid-resisting constituent contains an absorption-of-radiation component or a chromophore, a polymer binder and 1, or the cross linking agent beyond it. For example, the well-known acid-resisting constituent contained epoxy-phenol binder which does not have typically free hydroxyl, or the acrylate binder which does not have an acid radical substantially.

[0009] The variation in the topography (topography) of a base also produces the problem of the echo which restrains resolution. The image on a base may scatter about or reflect a collision radiation (impinging radiation) in the direction where versatility is not controlled, and affects the homogeneity of the development of a photoresist. If the topography of a base tends to design a more complicated circuit, it will become still more complicated and the effectiveness of the reflected radiation will become still more serious. For example, especially metal INTAKONEKUTO used on many micro electro nick bases is a problem because of the topography and a high reflexivity field.

[0010] One solution of the technical problem resulting from the variation in the topography of a base is the approach of arranging a photoresist in the height same on a front face, and the approach of this is indicated by U.S. Pat. No. 4557797 (Fuller et al.). The multilayer-structure object which has the comparatively thick lower layer of Pori (methylmetaacrylate) (PMMA) is used for this approach, and it offers a flat front face, the thin middle class who is antireflection coating, and the thin upper layer which

is the photoresist matter. However, this system forms as a result the thick polymer layer which must be removed. Typically, such a layer is removed by various approaches including chemical machinery polish (CMP), etching, and wet chemical \*\*. For the time amount of the addition by such clearance process, and cost, in order that a polymer layer may help subsequent clearance, a thing thin as much as possible is desired.

[0011] other solution of the technical problem accompanying the variation in the topography of a base -- Adams et al. and Planarizing AR for DUV Lithography and Microlithography 1999:Advances in Resist Technology and Processing XVI and Proceedings of SPIE vol.3678, part2, and pp849- it is indicated by 856 and 1999. This indicates the activity of the flattening antireflection coating which reduces the need of arranging a separate flattening layer between an acid-resisting layer and a base.

[0012] The activity of the photoresist layer to a dielectric layer top often brings about "poise NINGU" of a photoresist layer. This poses a problem, especially when a dielectric layer is applied by physics or chemical vacuum deposition (P/CVD). Although the theory of such poise NINGU is not understood thoroughly, such a dielectric layer may cause a remarkable photospeed shift (photospeed shift), lifting, degradation of a profile, or prohibition of the perfect dissolution in the beer field between trench daily rye NIEISHON [ in / already / an eclipse \*\*\*\*\* aperture field with a pattern, for example, a dual DAMASHIN process, ] (trench delineation). Such poise NINGU is a problem especially when a positive type photoresist like a deep UV (DUV) photoresist is used. Although BARC offered the effective chemical barrier to the photoresist layer, such its BARC was not fully effective for offering a barrier layer to such poise NINGU by the dielectric layer.

[0013] Therefore, offering the effective barrier to the PONIZUNINGU effectiveness of the photoresist by the dielectric layer, especially the need of receiving the barrier layer which offers the front face by which flattening was carried out exist.

[0014] It was found out that this invention decreases thru/or extinguishes the contamination or the poise NINGU effectiveness of a photoresist layer by the dielectric layer. It was also found out that the constituent of this invention forms a flat front face locally substantially. Furthermore, it was found out that this invention decreases thru/or extinguishes substantially the standing wave effectiveness, the Boeing (bowing), surface corrosion, and a footing (footing).

[0015] In the 1st mode, this invention is a barrier constituent containing the polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, and one or more solvents, and offers the polymer which can construct a bridge, and the constituent with which at least one of the cross linking agents has one or more acid parts.

[0016] In the 2nd mode, this invention is the approach of offering a barrier layer on a dielectric base, is a barrier constituent containing the polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, and one or more solvents, and offers an approach including the process which arranges the polymer which can construct a bridge, and the constituent with which at least one of the cross linking agents has one or more acid parts on the front face of a dielectric base.

[0017] In the 3rd mode, this invention is a device which has a dielectric layer and the barrier layer arranged on it, and offers the device with which this barrier layer has the polymer in which one or more bridge formation is possible as a polymerization unit, and one or more cross linking agents, and contains the polymer which can construct a bridge, and one or more polymers in which at least one of the cross linking agents has one or more acid parts, and over which the bridge was constructed.

[0018] In the 4th mode, include that this invention arranges a barrier layer between a dielectric layer and a photoresist layer. It is the approach of decreasing the contamination of a photoresist layer. This barrier layer has the polymer in which one or more bridge formation is possible as a polymerization unit, and one or more cross linking agents, and the approach containing the polymer which can construct a bridge, and one or more polymers in which at least one of the cross linking agents has one or more acid parts and over which the bridge was constructed is offered.

[0019] The process to which this invention offers a dielectric layer on a base in the 5th mode, b) The polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more

cross linking agents, And the barrier constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts including one or more solvents the process arranged on the front face of a dielectric layer, and c -- a base is heated to sufficient temperature to harden a barrier constituent selectively at least, and the manufacture approach including the process which forms a barrier layer of an electron device is offered.

[0020] The process to which this invention offers a dielectric layer on a base in the 6th mode, b) The polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, And the barrier constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts including one or more solvents A base is heated to sufficient temperature to harden a barrier constituent selectively at least. the process arranged on the front face of a dielectric layer, and c -- The manufacture approach including the process which forms a barrier layer, the process which arranges antireflection coating on the front face of d barrier layer, and the process which arranges a photoresist layer on the front face of e antireflection coating of an electron device is offered.

[0021] The :degree-C= Celsius degree;g= gram in which the following abbreviation has the semantics of a degree as what is used through this description unless it is shown especially in others; it is an engine-speed;%wt= percent-by-weight;mol%= mol %;mJ= Miri Joule;cm<sup>2</sup>= square centimeter;L= liter;mL= milliliter around for cm= cm;\*= angstrom;rpm= 1 minute. The vocabulary "a polymer" means a dimer, a trimer, a tetramer, oligomer, a homopolymer, a copolymer, etc. The vocabulary "a monomer" means the ethylene nature or the acetylene nature unsaturated compound of arbitration by which a polymerization can be carried out. Both acrylate and methacrylate are further included [ vocabulary / "an acrylic (meta)" ] with the vocabulary "acrylate (meta)" including both an acrylic and a meta-acrylic. Similarly, the vocabulary "acrylamide (meta)" means both acrylamide and meta-acrylamide. "Alkyl" contains a straight chain, branched chain, and a ring type alkyl group. A "cross linker" or a "cross linking agent" is used as an exchangeable thing in this description. "Aperture" means beer, trenches, and such combination. "A future (feature)" means various geometry including aperture. Unless it is shown especially in others, all amounts are percentage by weight and all ratios are weight ratios. Combination is possible for all numerical range including a boundary value.

[0022] This invention relates to offering the base which has a dielectric layer especially the dielectric layer PVD(ed) or CVD(ed), and a barrier layer. This invention relates to decreasing thru/or extinguishing poise NINGU or contamination of the photoresist by the dielectric layer, or an antireflection coating layer further. Especially this invention relates to the manufacture approach of an electron device that a photoresist, antireflection coating, or both were applied to the dielectric layer base.

[0023] The constituent of this invention is a barrier constituent containing the polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, and one or more solvents, and is useful as a barrier layer constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts. "An acid part" means one or more acidic groups which exist in the polymer which can construct a bridge, a cross linking agent, or its both. An acid part substantial more desirable completely does not contain a blocking radical preferably selectively at least. "Excluding a blocking radical", an acid part like the ether or ester which does not form the acidic group blocked by being organic-functions-ized or reacting is said. "Excluding a blocking radical substantially", 50% or more of an acid part is organic-functions-ized, or it says the acid part which does not form the acidic group blocked by reacting. desirable -- 30% or more of an acid part -- more -- desirable -- 20% or more -- organic functions -- it is-izing and carried out and the blocked acidic group is not formed. Although a carboxylic acid, a sulfonic acid, phosphonic acid, for example, a hydroxyl compound like an aromatic series hydroxyl compound, an acid anhydride, etc. are raised as such an acid part, it is not limited to these. It is desirable that an acid part contains an aromatic series hydroxyl compound.

[0024] It is desirable that the polymer which can construct a bridge contains the monomer which has one or more acid parts as a polymerization unit, and it is more desirable that one or more aromatic series

hydroxyl content monomers are included. the monomer which has an acid part in the polymer in which such bridge formation is possible -- typical -- about one to about 99-mol % -- desirable -- at least -- about three-mol % -- more -- desirable -- at least -- about five-mol % -- it exists in % of the amount of about ten mols at least further more preferably. As a polymer in which suitable bridge formation is possible, the thing containing the monomer which has about 20, 30, 40, 50, 60, 70 and 80, and a 90-mol % acid part at least as a polymerization unit is raised especially.

[0025] In this invention, the polymer and cross linking agent in which useful bridge formation is possible can also contain other functional groups. As other suitable functional groups, although an ester group, a halogen, cyano \*\* (C1-C6) ARUKOKISHI, etc. are raised, it is not limited to these. Such a polymer and a cross linking agent can also include the combination of more acid parts, for example, more aromatic series hydroxyls than 1, than 1 or aromatic series hydroxyl, and a carboxylic-acid radical.

[0026] Typically, the polymer which can construct a bridge has about 3000 or less weight average molecular weight more preferably about 5000 or less about 8000 or less. the polymer which can construct a bridge -- at least -- about 300 -- it is preferably desirable about 400 and to have about 500 weight average molecular weight at least more preferably at least. namely, especially the range of useful weight average molecular weight -- about 300 to about 8000 -- it is about 300 to about 5000 more preferably.

[0027] The polymer which can construct a bridge for this invention has small molecular weight and large molecular weight distribution. The molecular weight distribution of this invention are characterized as the polydispersed degree of a polymer, i.e., a ratio of weight average molecular weight and number average molecular weight, (Mw/Mn). the polymer of this invention -- typical -- at least 1.5 - - desirable -- at least 1.8 -- more -- desirable -- at least 2.0 -- further -- more -- desirable -- at least 2.5 -- further -- more -- at least 3.0 of a son-in-law -- it has most preferably, Mw/Mn, i.e., the polydispersed degree, of at least 3.5. the typical polydispersed degree of the polymer in which such bridge formation is possible -- 1.5 to 4 -- desirable -- 1.8 to 4 -- it is the range of 2 to 4 more preferably.

[0028] Although the polymer of the arbitration which has a polymerization unit of one or more hydroxyl content monomers like an aromatic aldehyde condensate and Pori (vinyl phenol) as a polymer in which suitable bridge formation is possible is raised, it is not limited to these. Although phenol novolak resin is mentioned as a useful aromatic series-aldehyde condensate in this invention, it is not limited to this. Such novolak resin is typically prepared by condensation with the aldehyde of a phenol, this novolak resin is still better known, and it is Kirk. Othmer Encyclopedia of Chemical It is indicated by many periodicals containing Technology, 15 volumes, 176-208 pages, and 1968, and the publication which teaches such resin in this periodical is referred to as some of these descriptions. Although a phenol is a phenol generally because of itself formation of such phenol resin used, and not limited especially for example, other hydroxy permutation aromatic compounds like bisphenols including p-phenylphenol and 4, and 4'-isopropylidene diphenol are suitable for alkylation phenol; lists including a resorcinol; naphthol, cresol, a xylenol, and p-tert-butylphenol similarly. Cresol is mentioned as desirable phenols and such mixture is more preferably mentioned to m-cresol, m- and the mixture of p-cresol, 2, 5-xylenol, and a list. The mixture of a hydroxy permutation aromatic compound can be advantageously used in this invention.

[0029] Although the aldehyde used is formaldehyde typically, and not limited to these, an acetaldehyde, furfuraldehyde, and other aldehydes like aromatic aldehyde can also be used, for example. Desirable aromatic aldehyde has hydroxyl in the ortho position of a carbonyl group. The most desirable aromatic aldehyde is salichlaldehyde, benzaldehydes, and those mixture. As other aromatic aldehyde suitable for the object of this invention, 2-chlorobenzaldehyde, 3-hydroxyl benzaldehyde, 4-hydroxyl benzaldehyde, 2-methoxy benzaldehyde, 3-nitro benzaldehyde, etc. are raised. The mixture of an aldehyde can also be used useful in this invention. When aromatic aldehyde is mixed with formaldehyde or a formaldehyde precursor, for example, a paraformaldehyde, rather than formaldehyde, the mol of aromatic aldehyde is superfluous, it exists and exists more preferably with at least 90% of the weight of aldehyde mixture.

[0030] Typically, phenol-novolak resin is \*\*\*\*\* (ed) from the aromatic compound and aldehyde by



which the hydroxyl permutation was carried out under existence of the condensation of a phenol, i.e., an acid. Although there can be less mol concentration of an aldehyde a little than the mol concentration of a phenol, it can be equivalent weight, and some [ of a phenol ] can also be superfluous without forming the resin which constructed the bridge. The ratio of a phenol and an aldehyde can change from this viewpoint from about 1.1 to 1.0 to 1.0 to 1.1. For example, refer to U.S. Pat. No. 5939511 (Zampini). general -- this invention -- setting -- such polydispersed degree of an aromatic series-aldehyde condensate useful as a polymer which can construct a bridge -- at least -- about 2.5 -- desirable -- at least -- about 3.0 -- it is about 3.5 at least more preferably.

[0031] The hydroxyl content ethylene nature or the acetylene nature unsaturated compound of arbitration is useful as a hydroxyl content monomer in this invention. Such a hydroxyl content monomer can be aliphatic series or aromatic series, and is aromatic series preferably. As a suitable hydroxyl content monomer A phenol, cresol, resorcinol, pyrogallol, a methylol phenol, Methylol cresol, methylol resorcinol, methylol pyrogallol, A hydroxyethyl phenol, a hydroxypropyl phenol, hydroxyethyl cresol, A vinyl phenol, vinyl cresol, a vinyl methoxy phenol, Hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 3-hydroxypropyl (meta) acrylate, hydroxy cyclohexyl (meta) acrylate, Hydroxyphenyl (meta) acrylate, G ethylene glycol (meta) acrylate, Although bis(hydroxyethyl) itaconate, bis (hydroxyethyl) citraconate, bis(hydroxyethyl) fumarate, hydroxyethyl itaconate, an allyl compound phenol, an allyl compound methoxy phenol, allyl alcohol, vinyl alcohol, etc. are raised It is not limited to these.

[0032] the polymer which can construct a bridge for this invention -- as a polymerization unit -- one or more aromatic compounds -- for example, -- at least -- about three-mol % -- desirable -- at least -- about five-mol % -- more -- desirable -- at least -- about ten-mol % -- containing is desirable. As a desirable aromatic compound, although a phenol nature compound, a cresol compound, a resorcinol compound, a xylenol compound, etc. are raised, it is not limited to these. As a polymer in which useful bridge formation is possible, what contains about 20-mol % of an aromatic compound at least as a polymerization unit is raised especially. It is still more desirable that the polymer which can construct a bridge contains one or more aromatic aldehyde condensates.

[0033] The values of Mw/Mn of an aromatic aldehyde condensate of especially the polymer in which useful bridge formation is possible are at least 2.5 and the thing which is at least 3.0 preferably including one or more aromatic aldehyde condensates and other one or more polymers, for example, (meta), an acrylate polymer. For example, (meta), the advantage which contains a non-aromatic polymer like an acrylate polymer with an aromatic aldehyde condensate is being, in case the etch rate of a barrier constituent is increased. It is still more desirable that the polymer which can construct a bridge for this invention does not include a sill phenylene part substantially, and it does not include a sill phenylene part more preferably.

[0034] Although an acrylic acid (meta), acrylamide (meta), alkyl (meta) acrylate, alkenyl (meta) acrylate, aromatic series (meta) acrylate, a vinyl aromatic series monomer, the thio analog of the nitrogen content compound another place, the permuted ethylene monomer are raised as a useful monomer in order to prepare the polymer which can construct a bridge for this invention, it is not limited to these. In this invention, the mixture of an aromatic aldehyde condensate is raised as a polymer in which useful especially desirable bridge formation is possible, and they are novolak resin and one or more mixture with Pori (meta) (acrylic acid), Pori (meta) (acrylamide), Pori (alkyl (meta) acrylate), Pori (alkenyl (meta) acrylate), Pori (aromatic series (meta) acrylate), and Pori (vinyl aromatic series) especially.

[0035] Typically, in this invention, useful alkyl (meta) acrylate is alkyl (C1-C24) (meta) acrylate. As suitable alkyl (meta) acrylate, although "low cut (low cut)" alkyl (meta) acrylate, "mid cut (mid cut)" alkyl (meta) acrylate, and "high cut (high cut)" alkyl (meta) acrylate are mentioned, it is not limited to these. Typically, as for "low cut" alkyl (meta) acrylate, an alkyl group has 1-6 carbon atoms. As suitable low cut alkyl (meta) acrylate, although it passes, and KISHIRU methacrylate is mentioned to KISHIRU methacrylate and cyclo and KISHIRU acrylate and such mixture are mentioned to cyclo, they are not a methylmetaacrylate (MMA), methyl acrylate, ethyl acrylate, propyl methacrylate, butyl methacrylate

(BMA), butyl acrylate (BA), isobutyl methacrylate (IBMA), and the thing limited to these.

[0036] Typically, as for "mid cut" alkyl (meta) acrylate, an alkyl group has 7-15 carbon atoms. As suitable mid cut alkyl (meta) acrylate To 2-ethyl to KISHIRU acrylate (EHA) and 2-ethyl KISHIRU methacrylate, Octyl methacrylate, decyl methacrylate, isodecyl methacrylate (it IDMA(s)) The undecyl methacrylate which uses branching (C10) alkyl isomer mixture as the base, Dodecyl methacrylate (known also as lauryl methacrylate), Although methacrylate, tetradecyl methacrylate (known also as milli still methacrylate), pentadecyl methacrylate, and such mixture are mentioned, it is not limited to these. As useful mixture, mixture [ of the dodecyl of dodecyl-pentadecyl methacrylate (DPMA), a straight chain, and branched chain, tridecyl, tetradecyl and pentadecyl methacrylate ]; and lauryl-millimeter still methacrylate (LMA) are mentioned especially.

[0037] Typically, as for "high cut" alkyl (meta) acrylate, an alkyl group has 16-24 carbon atoms. As suitable high cut alkyl (meta) acrylate, although hexadecyl methacrylate, heptadecyl methacrylate, octadecyl methacrylate, nona decyl methacrylate, KOSHIRU methacrylate, EIKO sill methacrylate, and such mixture are mentioned, it is not limited to these. Cetyl-EIKO sill methacrylate which is the mixture of hexadecyl, octadecyl, KOSHIRU, and EIKO sill methacrylate as especially useful mixture of high cut alkyl (meta) acrylate (CEMA); although the cetyl-stearyl metaacrylate (SMA) which is the mixture of hexadecyl and octadecyl methacrylate is mentioned to a list, it is not limited to these.

[0038] an above-mentioned MIDDO-cut -- and -- yes, - cut alkyl (meta) acrylate monomer is generally prepared by the standard esterification approach which used the long-chain fatty alcohol of reagent grade -- having -- these -- the alkyl group of available alcohol is 10-15 pieces or the mixture of various chain length's alcohol which it has 16-20 pieces about a carbon atom commercially. As an example of these alcohol, it is Vista. Chemical Various Ziegler catalyst-ized (Ziegler catalyzed) ALFOL alcohol from company, ALFOL1618 and ALFOL1620, Shell Chemical TA-1618 of Proctor&Gamble's and the alcohol of the natural product origin like CO-1270 are mentioned to various Ziegler catalyst-ized NEODOL alcohol from Company, i.e., NEODOL25L, and a list. [ i.e., ] Therefore, for the object of this invention, alkyl (meta) acrylate is meant with the thing also containing the mixture of the alkyl (meta) acrylate which each named alkyl (meta) acrylate product is not only included, but mainly contains the named specific alkyl (meta) acrylate.

[0039] In this invention, a useful alkyl (meta) acrylate monomer can be an independent monomer, or can be mixture with which the number of the carbon atoms of an alkyl part differs. Moreover, in this invention, useful acrylamide (meta) and a useful alkyl (meta) acrylate monomer can be permuted by arbitration. As the permutation (meta) acrylamide and the alkyl (meta) acrylate monomer of suitable arbitration, although hydroxy (C2-C6) alkyl (meta) acrylate, dialkylamino (C2-C6)-alkyl (meta) acrylate, and dialkylamino (C2-C6) alkyl (meta) acrylamide are mentioned, it is not limited to these. Especially a useful permutation alkyl (meta) acrylate monomer has one or more hydroxyls in an alkyl group, and hydroxyl is at least in beta- in an alkyl group especially (about 2-). The hydroxyalkyl (meta) acrylate monomer whose permutation alkyl group is the alkyl (C2-C6) of branched chain or a straight chain is desirable. As a suitable hydroxyalkyl (meta) acrylate monomer, although 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), 2-hydroxypropyl methacrylate, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxy-propylacrylate, 1-methyl-2-hydroxyethyl acrylate, 2-hydroxy butyl methacrylate, 2-hydroxy butyl acrylate, and such mixture are mentioned, it is not limited to these. Suitable hydroxyalkyl (meta) acrylate monomers are HEMA, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, and such mixture. Generally the mixture of the two latter monomers is called "hydroxypropyl methacrylate" or "HPMA."

[0040] In this invention, other useful acrylate (meta) and acrylamide (meta) monomers which were permuted have a dialkylamino radical or a dialkylamino alkyl group in an alkyl group. As an example of such permuted acrylate (meta) and acrylamide (meta) Dimethylaminoethyl methacrylate, dimethylamino ethyl acrylate, N and N-dimethylaminoethyl meta-acrylamide, N, and N-dimethyl-aminopropyl meta-acrylamide, N and N-dimethylamino butyl meta-acrylamide, N, and N-G ethylamino ethyl meta-acrylamide, N and N-diethylamino propyl meta-acrylamide, N, and N-diethylamino butyl meta-acrylamide, N-(1 and 1-dimethyl-3-oxo-butyl) acrylamide, N-(1 and 3-diphenyl-1-ethyl-3-oxo-butyl)

acrylamide, N-(1-methyl-1-phenyl-3-oxo-butyl) meta-acrylamide, And 2-hydroxyethyl acrylamide, N-meta-acrylamide of aminoethyl ethylene urea, Although such mixture is mentioned to N-METAAKURIRU oxy-ethyl morpholine, N-maleimide of dimethylamino propylamine, and a list, it is not limited to these.

[0041] Other permutation (meta) acrylate monomers useful to this invention gamma-pro PIRUTORI (C1-C6) alkoxy silyl (meth)acrylate, gamma-pro PIRUTORI (C1-C6) alkyl silyl (meth)acrylate, gamma-pro PIRUJI (C1-C6) alkoxy (C1-C6) alkyl silyl (meth)acrylate, gamma-pro PIRUJI (C1-C6) alkyl (C1-C6) alkoxy silyl (meth)acrylate, BINIRUTORI (C1-C6) alkoxy silyl (meth)acrylate, BINIRUJI (C1-C6) alkoxy (C1-C6) alkyl silyl (meth)acrylate, They are silicon content monomers, such as vinyl (C1-C6) ARUKOKISHIJI (C1-C6) alkyl silyl (meth)acrylate, BINIRUTORI (C1-C6) alkyl silyl (meth)acrylate, and such mixture.

[0042] Although styrene ("STY"), alpha methyl styrene, vinyltoluene, p-methyl styrene, ethyl vinylbenzene, vinyl naphthalene, vinyl xylenes, and such mixture are contained in a vinyl aromatic series monomer useful as a partial saturation monomer of this invention, it is not limited to these. Those corresponding permutation counterparts, such as derivative; containing one or more halogen radicals, such as a halogenated derivative, i.e., a fluorine, chlorine, or a bromine, and nitroglycerine, cyano \*\* (C1-C10) alkoxy \*\* halo (C1-C10) alkyl, Caleb (C1-C10) alkoxy \*\* carboxy, amino, and an alkylamino (C1-C10) derivative, are contained in a vinyl aromatic series monomer.

[0043] In a nitrogen content compound and a thio analog useful as a partial saturation monomer of this invention Vinylpyridines, such as a 2-vinyl-pyridine or 4-vinylpyridine; 2-methyl-5-vinylpyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2, 3-dimethyl-5-vinylpyridine, and low-grade alkyl (C1-C8) permutation N-vinylpyridine [, such as 2-methyl-3-ethyl-5-vinylpyridine, ]; -- methylation quinoline and isoquinoline; -- N-vinyl caprolactam; -- N-vinyl butyrolactam; -- N-vinyl-pyrrolidone; -- vinyl imidazole; -- N-vinylcarbazole; -- N-vinyl succinimide; (meta) -- acrylonitrile; -- o-, m-, or p-amino styrene; maleimide;N-vinyl oxazolidone;N -- N-dimethylaminoethyl-vinyl ether; -- ethyl-2-cyanoacrylate; -- vinylacetonitrile; -- N-vinyl phthalimide; -- an N-vinyl-thio-pyrrolidone -- A 3-methyl-1-vinyl-pyrrolidone, a 4-methyl-1-vinyl-pyrrolidone, A 5-methyl-1-vinyl-pyrrolidone, a 3-ethyl-1-vinyl-pyrrolidone, A 3-butyl-1-vinyl-pyrrolidone, 3, and 3-dimethyl-1-vinyl-pyrrolidone, A 4, 5-dimethyl-1-vinyl-pyrrolidone, 5, and 5-dimethyl-1-vinyl-pyrrolidone, 3, 3, a 5-trimethyl-1-vinyl-pyrrolidone, a 4-ethyl-1-vinyl-pyrrolidone, N-vinyl-pyrrolidone; vinyl pyrroles, such as a 5-methyl-5-ethyl-1-vinyl-pyrrolidone and 3 and 4, and 5-trimethyl-1-vinyl-pyrrolidone; although vinyl aniline; and a vinyl piperidine are contained, it is not limited to these.

[0044] this invention -- setting -- a permutation ethylene monomer useful as a partial saturation monomer -- allyl compound monomer, vinyl acetate, vinyl formamide, vinyl chloride, and vinyl fluoride, vinyl bromide, a vinylidene chloride, vinylidene fluoride, and bromination -- although a vinylidene acid is contained, it is not limited to these. The polymer which can construct a bridge exists in the amount of the broad range in the constituent of this invention. Typically, about 85% of polymers which can construct a bridge exists in about 60 to about 85% of amount preferably from about 40 of solid content.

[0045] In this invention, a useful cross linking agent is the matter of the polymer which can construct a bridge, and the arbitration which can perform acid-catalyst bridge formation. Typically, the cross linking agent of this invention has about 120dalton or the molecular weight beyond it. It is desirable that a cross linking agent performs crosslinking reaction at the temperature of about 75 to about 250 degrees C. Ji-, Tori -, a tetrapod, or a higher-order polyfunctional ethylene partial saturation monomer is contained in a suitable cross linking agent. as the example of a cross linking agent useful to this invention -- trivinylbenzene, divinyl toluene, divinyl pyridine, divinyl naphthalene, and divinyl xylene; -- and -- for example Ethylene glycol diacrylate, trimethylolpropane triacrylate, The diethylene-glycol divinyl ether, a TORIBI nil cyclohexane, Allyl compound methacrylate ("ALMA"), ethylene glycol dimethacrylate "EGDMA", Diethylene-glycol dimethacrylate ("DEGDMA"), propylene glycol dimethacrylate, Propylene glycol diacrylate, trimethylolpropanetrimethacrylate "TMPTMA", A divinylbenzene ("DVB"), glycidyl methacrylate, 2,2-dimethyl propane 1, 3 diacrylate, 1, 3-butylene-glycol diacrylate, 1,

3-butylene-glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, Diethylene-glycol dimethacrylate, 1,6-hexanediol diacrylate, 1, 6-hexanedioldimethacrylate, tripropylene glycol diacrylate, Triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, Polyethylene-glycol 200 diacrylate, tetraethylene glycol dimethacrylate, Polyethylene glycol dimethacrylate, ethoxyl-ized bisphenol A diacrylate, Ethoxyl-ized bisphenol A dimethacrylate, polyethylene-glycol 600 dimethacrylate, Pori (butanediol) diacrylate, a pentaerythritol thoria chestnut rate, Trimethylolpropane triethoxyacrylate, glyceryl propoxy thoria KURIRETO, Pentaerythritol tetraacrylate, pentaerythritol tetra-methacrylate, Dipentaerythritolmonohydroxypentaacrylate, a divinyl silane, A TORIBI nil silane, a dimethyl divinyl silane, divinyl methylsilane, A methyl TORIBI nil silane, a diphenyl divinyl silane, divinyl phenylsilane, TORIBI nil phenylsilane, a divinyl methylphenyl silane, a tetravinyl silane, Dimethyl vinyl disiloxane, Pori (methylvinyl siloxane), Pori (vinyl hydronalium siloxane), Although Pori (phenyl vinyl siloxane), tetramethoxy glycoluryl, tetrapod (C1-C8) alkoxy glycoluryl like tetra-butoxy glycoluryl, and such mixture are raised, it is not limited to these.

[0046] The cross linking agent of this invention exists in the amount of the broad range in the constituent of this invention. Typically, about 25% of cross linking agents exists [ 10 / about ] in about 15 to about 25% of amount more preferably about 30% from about 1 of solid content. In this invention, a useful acid catalyst is the thing of the arbitration which can carry out the catalyst of the crosslinking reaction of the barrier layer constituent of this invention, and a free acid (free acid) and an acid formation agent (acid generator) are raised. As an example of a free acid, although methansulfonic acid, ethane sulfonic acid, a propyl sulfonic acid, a phenyl sulfonic acid, toluenesulfonic acid, dodecylbenzenesulfonic acid, and trifluoro methylsulfonic acid are raised, it is not limited to these.

[0047] As an acid formation agent, a heat acid formation agent (TAG), photograph acid formation agents (PAG), and those mixture are raised. The heat acid formation agent and photograph acid formation agent of arbitration are useful in this invention. A heat acid formation agent is the compound of the arbitration which separates an acid by heat treatment. As a suitable heat acid formation agent, although 2, 4, 4, 6-tetrabromo cyclohexa JIENON, benzoin tosylate, 2-nitrobenzyl tosylate and the alkyl ester of other organic sulfonic acids, and the amine salt of a sulfonic acid, for example, the amine salt of dodecylbenzenesulfonic acid, are raised, it is not limited to these. Generally activation, i.e., the thing which generates a sulfonic acid by exposure to heat, is desirable. A photograph acid formation agent is a compound which separates an acid by the photolysis. As a suitable photograph acid formation agent, it is onium salt and halogenation nonionic photograph acid formation agent, 1 [ for example, ], and 1-screw (p-chlorophenyl). - Although 2, 2, and 2-trichloroethane and a fluoro alkyl sulfonic acid like a perfluoro-octyl sulfonic acid are raised, it is not limited to these.

[0048] 8% of acid catalysts exists preferably in the constituent of this invention typically in about 0.5 to about 5% of amount of solid content from about 0.1 of sufficient amount, for example, solid content, to carry out the catalyst of the desired crosslinking reaction. It is desirable in this invention to use the combination of an acid catalyst. As a suitable combination, a free acid and a heat acid formation agent are raised to a free acid, a photograph acid formation agent, and a list. Generally it is known, such an acid catalyst is commercially available, and it can be used, without refining further.

[0049] The constituent of this invention contains one or more solvents. The solvent of the arbitration of compatibility with a compound is suitable. The solvent of hypoviscosity is desirable. As a suitable solvent, for example Propylene glycol methyl ether acetate, 2-heptanone, ethyl lactate, or one or more glycol ether, For example, 2-methoxy ethyl ether (jig lime), ethylene glycol monomethyl ether, Propylene glycol monomethyl ether; The solvent which has both an ether part and a hydroxy part, For example, methoxybutanol, an ethoxy butanol, methoxy propanol, And ethoxy propanol; Ester, for example, methyl-cellosolve acetate, Ethylcellosolve acetate, propylene-glycol-monomethyl-ether acetate, Although dipropylene-glycol-monomethyl-ether acetate and other solvents, for example, dibasicity ester, propylene cull BONETO, a gamma-butyrolactone, etc. are raised, it is not limited to these. this invention -- setting -- especially a useful suitable solvent -- a comparison -- it is the high boiling point, i.e., the solvent which has at least preferably about 170 degrees C of about 190-degree C boiling points at least. The mixture of a solvent can also be used useful in this invention. That is, the

solvent of this invention is mixable with other one or more solvents. Such other solvents can be a high-boiling point or a low-boiling point. When two or more solvents are used, it is desirable that at least one solvent has the boiling point of the range of about 75 to about 200 degrees C. When two or more solvents are used, it is desirable that at least one solvent has less than about 200 boiling point, and has the boiling point when other at least one solvent is more expensive than about 200 degrees C.

[0050] Although the constituent of this invention is not limited to arbitration by other one or more components and these, it can contain a plasticizer, a surfactant, a lubricating agent, a color, a chromophore, a pigment, etc., for example. A plasticizer can be added to the constituent of this invention in order to improve the specific property of a constituent. Although dibasic ester like a dimethyl horse mackerel peat and dimethyl succinate is raised as a suitable plasticizer, it is not limited to these. The mixture of a plasticizer can be used in this invention. Typically, a plasticizer is preferably used in about 1 to about 5% of amount about 10% from about 0.5 of solid content. It is desirable that one or more plasticizers are used in this invention. up to about 50% of solid content -- since -- it is understood by this contractor that a lot of plasticizers like about 100% are used useful in this invention - - I will come out. As for a plasticizer, it is desirable that it is a liquid.

[0051] As a surface active agent of arbitration, although a nonionic surfactant, cationic surface active agents, and those mixture are raised, it is not limited to these. That to which especially a suitable surfactant is sold from a fluorination surfactant, for example, 3M company, is raised. A surfactant is typically used in about 0.1 to about 1.0% of the weight of the range.

[0052] It is surface leveling agents including what is available as a trade name Silwet7604 from Witco as an advantageous leveling agent in this invention, or 3M. The available surfactant FC430 is mentioned from Company. Selection and the amount of such a leveling agent are the matter of this contractor's capacity within the limits. Typically, such a leveling agent is used in about 0.1 to about 2% of amount of the total solid content.

[0053] The constituent of this invention can act also as antireflection coating. For example, when the polymer and/or cross linking agent which can construct a bridge contain an aromatic series radical, such a constituent can be used as an acid-resisting constituent to 193nm radiation. As an exception method, a color or a chromophore can be added to the constituent of this invention by copolymerization or mixing, and a useful acid-resisting constituent can be offered in the radiation of other wavelength. For example, sufficient chromophore for the polymer and/or cross linking agent which can construct a bridge is made to contain, and about 0.3 to about 0.8 optical density can be obtained in the exposure wavelength used for the photoresist layer applied succeedingly. As an exception method, a chromophore like an anthracene compound can be directly added to the constituent of this invention.

[0054] The concentration of the concentration of the desiccation component in a solvent, i.e., the polymer in which one or more bridge formation is possible, one or more acid catalysts, and one or more cross linking agents changes according to the factor of many like the method of application. Generally, the solid content content of the constituent of this invention is about 0.5 to 25 of the sum total weight of a constituent % of the weight, and a solid content content is about 2 to 20 of the sum total weight of a constituent % of the weight preferably. The constituent of this invention is prepared by combining a component in order of arbitration.

[0055] The constituent of this invention is useful as a barrier layer on a base, especially a dielectric layer base in manufacture of an electron device, for example, a semi-conductor, a conductor, an integrated circuit, a printed circuit board, etc. The constituent of this invention is useful especially in manufacture of a semiconductor device like the wafer used in manufacture of a semi-conductor. The constituent of this invention is applicable to a base by the various approaches of arbitration like for example, spin coating. In case it applies to a base, the constituent of this invention offers coating or the layer arranged on a base front face. For example, when a constituent is applied to a semi-conductor wafer by spin coating, about 1.5 microns of thickness of the film obtained can be preferably controlled in about 200Å to about 1.5 microns from less than about 200Å. Typically, about 1600Å of barrier constituents of this invention is preferably applied in an about 600 to 1200Å layer from about 600.

[0056] That is, this invention is the approach of offering a barrier layer on a dielectric base, is a barrier

constituent containing the polymer in which one or more bridge formation is possible, one or more acid catalysts, one or more cross linking agents, and one or more solvents, and offers an approach including the process which arranges the polymer which can construct a bridge, and the constituent with which at least one of the cross linking agents has one or more acid parts on the front face of a dielectric base.

[0057] In the photoresist of arbitration by the dielectric layer of arbitration, and the dielectric layer by which PVD(ing) or CVD deposition was carried out preferably, or contamination of antireflection coating, the barrier layer of this invention is advantageously used, reduction thru/or in order to lose. As a suitable dielectric layer, an inorganic dielectric layer, organic dielectric layers, and such mixture are raised, and it is an inorganic dielectric layer preferably. As a suitable inorganic dielectric layer, although silicon content dielectric layers, such as a silica, SHIRUSE float oxane (silsesquioxanes), alkoxysilane by which condensation was carried out selectively, and silicate by which refining was carried out organically, are raised, it is not limited to these. Various organic dielectric matter can also be used in this invention.

[0058] Typically, a bridge is selectively constructed over the constituent of this invention at least by heating about 250 degrees C at about 90 to about 225 degrees C preferably from about 75. The thing of a barrier constituent for which a bridge is constructed over about 10% at least is said [ "a bridge is constructed selectively at least" and ]. It is desirable that a bridge is substantially constructed over a barrier constituent, and a bridge is more preferably constructed over it thoroughly. The constituent of this invention can be hardened by presenting one process or 2 process baking with the base by which coating was carried out with the constituent. The constituent of temperature and a period sufficient in 1 process baking to construct a bridge in a constituent substantially preferably selectively at least, and this invention is heated. As an exception method, although 2 process baking is not enough to construct a bridge in a constituent, it heats to the 1st temperature which is made to carry out a reflow of the constituent and improves smooth nature, and the constituent of the 2nd sufficient temperature and a sufficient period to construct a bridge in a constituent substantially preferably selectively at least subsequently, and this invention is heated.

[0059] Generally, the constituent of this invention is more preferably hardened [ 15 / about / 30 / about ] for about 60 seconds further more preferably for about 120 seconds for about 120 seconds for about 360 seconds from about 15. It will be understood by this contractor that the concrete setting time changes with whenever [ class / of cross linking agent /, amount / of a cross linking agent /, amount / of an acid catalyst /, and stoving temperature ] etc. This invention is a device which has further a dielectric layer and the barrier layer arranged on it, and offers the device with which this barrier layer has the polymer in which one or more bridge formation is possible as a polymerization unit, and one or more cross linking agents, and contains the polymer which can construct a bridge, and one or more polymers in which at least one of the cross linking agents has one or more acid parts, and over which the bridge was constructed. In such a device, it is desirable that the photoresist layer is arranged on a barrier layer. It is still more desirable that an acid-resisting constituent is arranged between a barrier layer and a photoresist layer.

[0060] In manufacture of an electron device, especially a semi-conductor wafer, a dielectric layer is often applied by a physical vapor deposition (PVD) or chemical vacuum deposition (CVD). Because of continuing etching and a metallization process, eclipse \*\*\*\*\* with a pattern is required for these dielectric layers. Such pattern NINGU is attained by the activity of a photoresist and is often used with antireflection coating. Application of the layer of the barrier constituent of this invention before applying a photoresist layer, and the application before applying antireflection coating preferably decrease or lose poise NINGU or contamination of a photoresist layer by the dielectric layer.

[0061] Poise NINGU or contamination of a photoresist layer is proved by reduction of the resolution of a future. For example, drawing 1 is the cross-section photograph of scanning electron microscope (SEM) \*\* of the contact hole in the dielectric layer formed without using a barrier layer. The remarkable Boeing in the pars basilaris ossis occipitalis of a contact hole is clearly seen in this drawing. When the barrier layer of this invention is used, it decreases greatly or poise NINGU or contamination of a photoresist layer is canceled so that it may be shown by the Boeing. Drawing 2 is the cross-section

photograph of the scanning electron microscope (SEM) of the contact hole in the dielectric layer formed using the barrier layer of 600A this invention. As compared with drawing 1, reduction of the amount of the Boeing in the pars basilaris ossis occipitalis of a contact hole is seen clearly. If the barrier layer of this invention becomes thicker, such poise NINGU or contamination will decrease further. 5 is the cross-section photograph of the scanning electron microscope (SEM) of the contact hole in the dielectric layer formed using thickness (1000A, 1500A, and 2000A) of the barrier layer, respectively from drawing 3. As shown in drawing 2 thru/or 5, the barrier layer of this invention decreases poise NINGU or contamination of a photoresist layer notably so that it may be shown by the Boeing.

[0062] The polymer for which this invention constructs [ the process which offers a dielectric layer on a base and ] beyond b1 a bridge, The barrier constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts including one or more acid catalysts, one or more cross linking agents, and one or more solvents the process arranged on the front face of a dielectric layer, and c -- a base is heated to sufficient temperature to harden a barrier constituent selectively at least, and the manufacture approach including the process which forms a barrier layer of an electron device is offered. Typically, a photoresist layer is arranged on the front face of a barrier layer. It is desirable that antireflection coating is arranged between the front face of a barrier layer and the front face of a photoresist layer. It is still more desirable that a photoresist layer contains a positive type photoresist.

[0063] The polymer for which this invention constructs [ the process which offers a dielectric layer on a base and ] beyond b1 a bridge, The barrier constituent with which at least one of the polymer which can construct a bridge, and the cross linking agents has one or more acid parts including one or more acid catalysts, one or more cross linking agents, and one or more solvents A base is heated to sufficient temperature to harden a barrier constituent selectively at least. the process arranged on the front face of a dielectric layer, and c -- The manufacture approach including the process which forms a barrier layer, the process which arranges antireflection coating on the front face of d barrier layer, and the process which arranges a photoresist layer on the front face of e antireflection coating of an electron device is offered.

[0064] When the barrier layer of this invention is used without using antireflection coating, a barrier layer is more desirable about 1000A at least, and it is desirable to have the thickness of about 1500A at least further more preferably about 1200A at least. When antireflection coating is arranged between a barrier layer and a photoresist layer, it is desirable that a barrier layer has at least more preferably about 400A of thickness of about 600A at least. About 2000A of the typical range of about 2500A of the thickness of the barrier is about 800 to 1500A more preferably in about 600 from about 400. Generally, antireflection coating has preferably about 2000A of thickness of about 400 to about 1600A from about 200. Generally a photoresist layer has preferably about 10000A of thickness of about 500 to about 7500A from about 200.

[0065] The advantage of the constituent of this invention is that they are a photoresist, and the dielectric and spin ball compatibility (spin bowl compatible). [ SUPINON / compatibility ] Although this invention was explained about semi-conductor manufacture, this invention can be used in a broad application. The following examples do not illustrate the various modes of this invention, and do not restrict the range of this invention at all.

[0066] the :metacresol-Parakou resol -2 by which the example 1 barrier layer constituent was prepared by combining the following, and 5-dimethoxy phenol novolak polymer (the solution of 30% of solid content in propylene-glycol-monomethyl-ether acetate (PGMEA) --) 301.268g and 75.95% of solid content, Mn800, Mw2500 g/mol, Tg83 degree C; 9.520g of dodecylbenzenesulfonic acid blocked as a heat acid formation agent, King Industries, Norwalk, and Connecticut -- since -- Nacure5225 sold and 25% solid content in isopropanol -- 2% of solid content; it is tetra-butoxy glycoluril (26.180g) as a cross linking agent. 22% of solid content; surface activity lubricating agent FC430 (it is sold from 3M, Minneapolis, and Minnesota) 1% solution in PGMEA, 5.950g, 0.05% of solid content; dimethyl horse mackerel peat (5.950g, 5% of solid content which does not contain this);, and 322.512g of PGMEA. This obtained sample of 17% of solid content 700g. enough to dissolve the matter in a constituent --



carry out a time amount roll (roll) and let the 0.2-micron Pori (tetrafluoroethylene) (PTFE) filter pass before an activity -- it passed.

[0067] It is called four wafers (sample 1-4) containing an example 2 P/CVD dielectric layer. Mark8 was used and the spin coat was carried out by various thickness with the barrier constituent of an example 1. The constituent was baked for 60 seconds at 195 degrees C. Spin coating of the commercial antireflection coating (AR7, Shipley Company, Marlborough, product made from Massachusetts) was carried out on the front face of the hardened barrier constituent, and it considered as the thickness of 600A, subsequently it baked for 60 seconds at 175 degrees C, and the film was hardened. Spin coating was carried out by the same thickness various with AR7 antireflection coating, and four wafers (comparison sample C1-C4) which have the same P/CVD dielectric layer were baked on the same conditions. These comparison samples do not contain the barrier constituent. Spin coating of all the wafers was carried out by the commercial photoresist (UV210, product made from Shipley Company). Coating of the photoresist was carried out to the thickness of 5000A, and it was baked for 60 seconds at 130 degrees C. Subsequently, the wafer used ASML 5500/200, and exposed it by 25 mJ/cm<sup>2</sup> to 33 mmJ/cm<sup>2</sup>, and the trench whose aspect ratio is 200nm of 1:2 was prepared. Succeedingly, at 130 degrees C, the wafer was baked for 90 seconds to exposure, and, subsequently was developed to it. A result is shown in a table 1.

[0068]

[A table 1]

表 1

サンプル	バリア組成物 厚さ (Å)	反射防止コーティング 厚さ (Å)	露光結果
1	1300	600	イメージされた
2	1000	600	イメージされた
3	700	600	イメージされた
4	400	600	イメージされた
C-1	0	1300	イメージされなかった
C-2	0	1000	イメージされなかった
C-3	0	1600	ほとんど識別できない イメージであった
C-4	0	1900	イメージされたが、最小 照射量ではなかった

[0069] The above-mentioned data show clearly that it is effective in the barrier constituent of this invention decreasing in number or preventing poise NINGU or contamination of a photoresist layer by the dielectric layer. Furthermore, in case the constituent of this invention is used, the thickness of an antireflection coating layer can be decreased.

[0070] The spin coat of the four wafers (sample 5-8) which have example 3P / CVD dielectric layer was carried out by thickness various with the barrier constituent of an example 1. The constituent was baked for 60 seconds at 205 degrees C. Spin coating of the commercial antireflection coating (AR3, product made from Shipley Comapany) was carried out on the front face of the hardened barrier constituent, and it considered as the thickness of 600A, subsequently it baked for 60 seconds at 205 degrees C, and the film was hardened. Similarly spin coating was carried out by the thickness of 600A by AR3 antireflection coating, and one wafer (comparison sample C5) which has the same P/CVD dielectric layer was baked on the same conditions. These comparison samples do not contain the barrier constituent. Spin coating of each wafer was carried out by the commercial photoresist (UV200, product made from Shipley Company). Coating is carried out to the thickness of 5000A, and a photoresist is a pro squeak tee. The hot plate (proximity hotplate) was used and it was baked for 60 seconds at 140



degrees C. Subsequently, the wafer was exposed using ASML 5500/300, and prepared the 0.22-micron contact hole. They are 90 seconds and a pro squeak tee at 140 degrees C about a wafer succeedingly to exposure. It baked using the hot plate and, subsequently negatives were developed. The scanning electron microscope (SEM) estimated the wafer after development. Drawing 15 shows the sectional view of the formed contact hole. Exposure conditions and a result are shown in a table 2.

[0071]

[A table 2]

表 2

サンプル	バリア組成物 厚さ (Å)	$E_0$ (mJ/cm <sup>2</sup> )	$E_s$ (mJ/cm <sup>2</sup> )	図
5	600	5.0	33.0	2
6	1000	5.0	29.5	3
7	1500	5.0	34.5	4
8	2000	5.0	33.0	5
C-5	0	5.9	-	1

[0072] The activity of the barrier constituent of this invention offers a contact hole with little a good sidewall profile (sidewall definition) and the Boeing as compared with what was formed without using a barrier constituent. For example, drawing 1 is the cross-section photograph of the contact hole by the comparison sample C-5, and this shows the remarkable Boeing. By contrast, drawing 25 is the cross-section photograph of the contact hole formed using the barrier constituent of this invention. These photographs show clearly that a contact hole has a good sidewall profile and has little Boeing intentionally.

[Translation done.]

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DRAWINGS

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[Drawing 1]

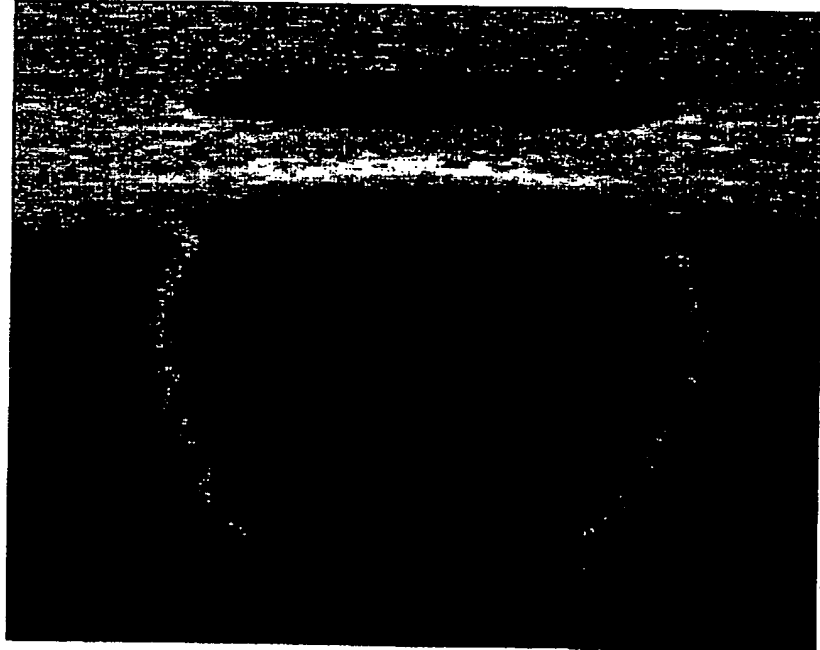


図 1

[Drawing 2]

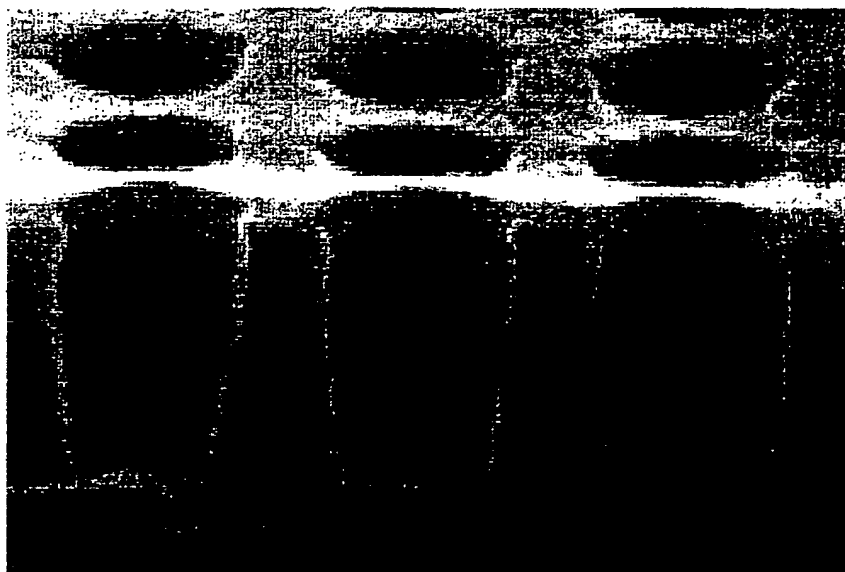


図 2

[Drawing 3]



図 3

[Drawing 4]

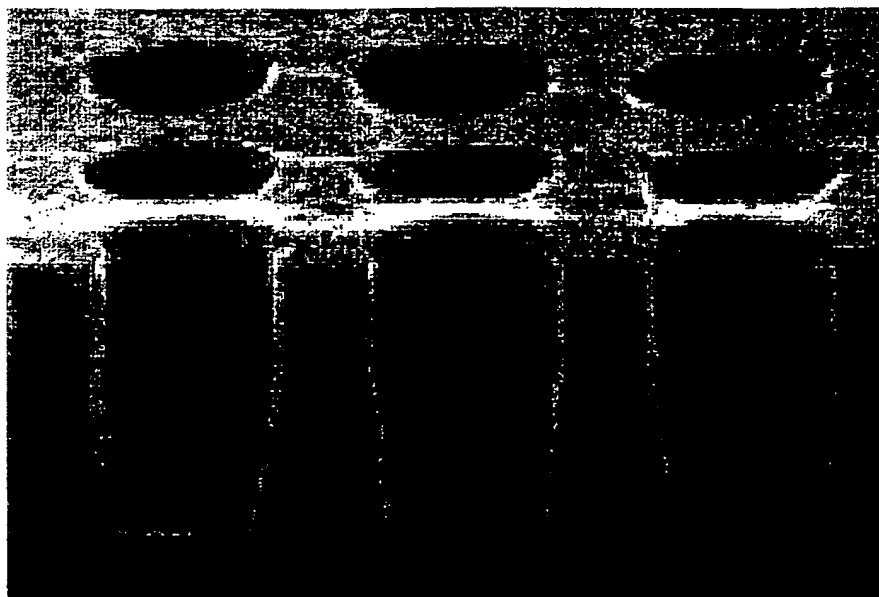


図 4

[Drawing 5]

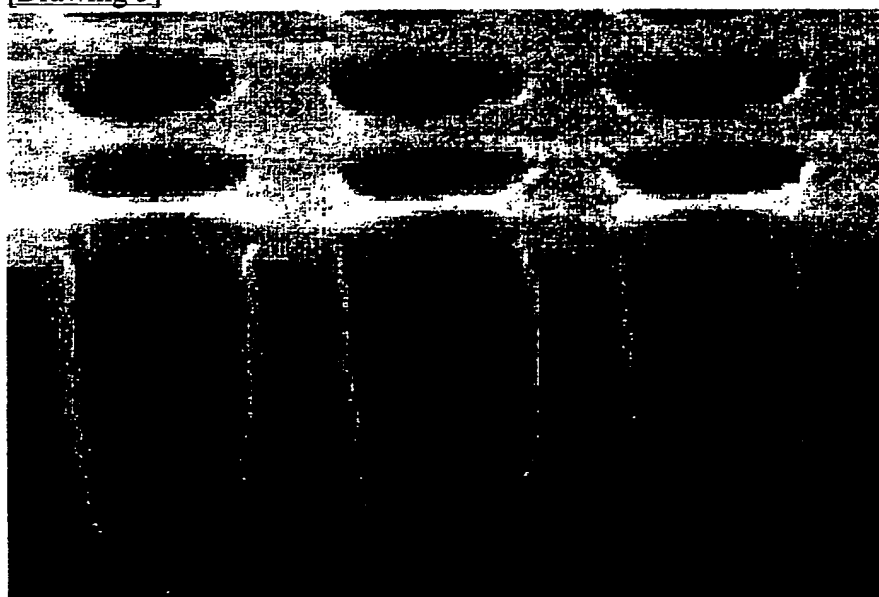


図 5

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[Translation done.]

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(54) 【発明の名称】 バリア組成物

(57) 【要約】

電子デバイス製造において使用されるバリア層を提供するための組成物および方法が開示される。また、電子デバイス製造におけるフォトレジストのボイズニングを減少または解消する方法が開示される。

## 【特許請求の範囲】

【請求項1】1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含むバリア組成物であって、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する、組成物。

【請求項2】架橋可能なポリマーが重合単位として1以上の芳香族ヒドロキシル化合物を有する、請求項1記載の組成物。

【請求項3】架橋可能なポリマーが1以上の芳香族アルデヒド縮合物を含む、請求項1記載の組成物。

【請求項4】酸性部位が少なくとも部分的にブロッキング基を含まない、請求項1記載の組成物。

【請求項5】架橋可能なポリマーが1以上の芳香族アルデヒド縮合物、および1以上の（メタ）アクリレートポリマーを含む、請求項1記載の組成物。

【請求項6】誘電体基体上にバリア層を提供する方法であって、1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含む組成物であって、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する組成物を、誘電体基体の表面上に配置する工程を含む、方法。

【請求項7】架橋可能なポリマーが重合単位として1以上の芳香族ヒドロキシル化合物を含む、請求項6記載の方法。

【請求項8】架橋可能なポリマーが1以上の芳香族アルデヒド縮合物を含む、請求項6記載の方法。

【請求項9】酸性部位が少なくとも部分的にブロッキング基を含まない、請求項6記載の方法。

【請求項10】架橋可能なポリマーが1以上の芳香族アルデヒド縮合物、および1以上の（メタ）アクリレートポリマーを含む、請求項6記載の方法。

【請求項11】誘電体基体が物理蒸着または化学蒸着により適用される、請求項6記載の方法。

【請求項12】誘電体基体が無機物である、請求項6記載の方法。

【請求項13】誘電体基体が珪素を含む、請求項6記載の方法。

【請求項14】誘電体層とその上に配置されるバリア層を有するデバイスであって、該バリア層が、重合単位として1以上の架橋可能なポリマー、および1以上の架橋剤を有し、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する、1以上の架橋されたポリマーを含む、デバイス。

【請求項15】さらにフォトレジスト層を有する、請求項14記載のデバイス。

【請求項16】バリア層とフォトレジスト層の間に配置された、反射防止コーティングをさらに含む、請求項14記載のデバイス。

【請求項17】バリア層が約200オングストロームから約1.5ミクロンまでの厚さを有する、請求項14記

載のデバイス。

【請求項18】誘電体層が物理蒸着または化学蒸着により適用される、請求項14記載のデバイス。

【請求項19】誘電体層が無機物である、請求項14記載のデバイス。

【請求項20】誘電体層が珪素を含む、請求項14記載のデバイス。

【請求項21】誘電体層とフォトレジスト層の間にバリア層を配置することを含む、フォトレジスト層のコンタミネーションを減少させる方法であって、該バリア層が、重合単位として1以上の架橋可能なポリマー、および1以上の架橋剤を有し、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する、1以上の架橋されたポリマーを含む、方法。

【請求項22】架橋可能なポリマーが重合単位として1以上の芳香族ヒドロキシル化合物を含む、請求項21記載の方法。

【請求項23】架橋可能なポリマーが1以上の芳香族アルデヒド縮合物を含む、請求項21記載の方法。

【請求項24】酸性部位が少なくとも部分的にブロッキング基を含まない、請求項21記載の方法。

【請求項25】架橋可能なポリマーが1以上の芳香族アルデヒド縮合物、および1以上の（メタ）アクリレートポリマーを含む、請求項21記載の方法。

【請求項26】誘電体基体が無機物である、請求項21記載の方法。

【請求項27】誘電体基体が珪素を含む、請求項21記載の方法。

【請求項28】バリア層が約200オングストロームから約1.5ミクロンまでの厚さを有する、請求項21記載の方法。

【請求項29】a) 基体の上に誘電体層を提供する工程、

b) 1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含み、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア組成物を、誘電体層の表面上に配置する工程、

c) 少なくとも部分的にバリア組成物を硬化するに十分な温度に基体を加熱し、バリア層を形成する工程、を含む、電子デバイスの製造方法。

【請求項30】a) 基体の上に誘電体層を提供する工程、

b) 1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含み、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア組成物を、誘電体層の表面上に配置する工程、

c) 少なくとも部分的にバリア組成物を硬化するに十分な温度に基体を加熱し、バリア層を形成する工程、

d) バリア層の表面に反射防止コーティングを配置する工程、

e) 反射防止コーティングの表面にフォトレジスト層を配置する工程、

を含む、電子デバイスの製造方法。

【発明の詳細な説明】

【0001】本発明は一般に電子デバイスの製造に関する。より詳細には、本発明は電子デバイスの製造において使用されるフォトレジストおよび反射防止コーティングに関する。

【0002】プリント基板または半導体などの電子デバイスの製造においては、フォトレジストまたは反射防止コーティングなどの多くの物質の層が基体上に適用される。フォトレジストは基体へイメージを転写するのに用いられる感光性フィルムである。フォトレジストのコーティング層を基体上に形成し、フォトレジスト層を次にフォトマスク（レチクル（reticle））を通して活性放射線源で露光する。フォトマスクは活性放射線に対して不透過性の領域と、活性放射線に対して透過性の他の領域を有する。活性放射線で露光すると、フォトレジストコーティングの光により誘発された化学的転換が起こり、フォトマスクのパターンが基体を覆うフォトレジストに転写される。露光後、フォトレジストを現像してレリーフイメージを得、これにより基体の選択的加工が可能になる。

【0003】フォトレジストはポジ型またはネガ型のいずれかであることができる。ほとんどのネガ型フォトレジストについて、活性放射線で露光されるこれらのコーティング層部分は、フォトレジスト組成物の光活性化化合物（photoactive compound）と重合性試薬間の反応において重合するかまたは架橋する。したがって、露光されたコーティング部分は未露光部分よりも現像液中に溶けにくい。ポジ型フォトレジストについては、露光された部分は現像液中により溶けやすくなるが、未露光部分は比較的現像液に溶けにくいままである。フォトレジスト組成物は当業界で公知であり、Deforest, Photoresist Materials and Processes, McGraw Hill Book Company, New York, 第2章、1975およびMoreau, Semiconductor Lithography, Principles, Practices and Materials, Plenum Press, New York, 第2章および第4章（いずれもフォトレジスト組成物とその製造法および使用法を記載する部分が本発明の一部として参照される）に記載されている。

【0004】フォトレジストの主な用途は、半導体製造における使用であり、その目的はビア、トレンチまたはそれらの組み合わせのような構造を、誘電体層に形成することである。適切なフォトレジスト加工がこの目的を

達成するために重要である。種々のフォトレジスト加工工程間には強力な相互依存性があるが、露光は高分解能フォトレジストイメージを得る、より重要な工程の一つであると考えられる。

【0005】そのようなプロセスにおいて、フォトレジストの露光の間における活性放射線の反射、および誘電体層によるフォトレジストの「ポイズニング（poisoning）」は、微細な構造の形成のために有害である。たとえばフォトレジストの下層からの活性放射線の反射は、フォトレジスト層においてパターン化されたイメージの分解能を制約することが多い。基体／フォトレジスト界面からの放射線の反射は、露光中にフォトレジスト内の放射線強度を変動させることができ、その結果、現像時にフォトレジストのライン幅が不均一になる。放射線はさらに基体／フォトレジスト界面から、露光する意図のないフォトレジスト領域中に散乱することができ、これによってもライン幅の変動が生じる。散乱および反射量は典型的には場所によって異なり、その結果、さらにライン幅が不均一になる。

【0006】活性放射線の反射はさらに「定在波効果（standing wave effect）」として当業界で知られる現象の一因となる。露光装置のレンズにおける色収差の効果もなくすために、フォトレジスト投影技術において単色または準単色放射線が通常用いられる。しかしながら、フォトレジスト／基体界面での放射線の反射のために、単色または準単色放射線をフォトレジスト露光に用いる場合に、強め合う干渉および弱め合う干渉が特に著しい。このような場合、反射された光は入射光と干渉し、フォトレジスト内に定在波を形成する。高反射性基体領域の場合においては、振幅の大きな定在波の極小点で露光不足の（underexposed）フォトレジストの薄層を形成するので問題は悪化する。露光不足の層は完全なフォトレジストの現像を妨げることができ、フォトレジストプロフィールにおいてエッジアキュティー（edge acuity）の問題が生じる。フォトレジスト量が増大するとこれを露光するために要する放射線の総量が増大するので、フォトレジストを露光するために要する時間は一般にフォトレジストの厚さの増加関数である。しかしながら、定在波効果のために、露光の間は、フォトレジストの厚さ方向において、連続して最大値と最小値間で変化する高調波（harmonic component）を含む。フォトレジストの厚さが不均一である場合、問題はさらに深刻になり、ライン幅が変動する。

【0007】高密度半導体デバイスへの最近の指向により、産業界において深紫外（DUV）光（波長が300 nm以下）、KrFエキシマレーザー光（248 nm）、ArFエキシマレーザー光（193 nm）、電子線および軟X線のように露光光源の波長を短くする動きがある。フォトレジストコーティングのイメージ化に波

長を短くした光を用いることにより、一般に、レジスト上部表面ならびに下部基体表面からの反射が増大する。このように、より短い波長の使用は基体表面からの反射の問題を悪化させる。

【0008】反射された放射線の問題を低減するために用いられるさらなる方法は、基体表面とフォトレジストコーティング層の間にある、ボトム反射防止コーティングまたはBARCと称する放射線吸収層、またはフォトレジストコーティングの表面上に配置される、トップ反射防止コーティングまたはTARCと称する放射線吸収層を使用することであった。例えば、PCT出願WO90/03598号、欧州特許出願第0639941A1号および米国特許第4910122号、第4370405号および第4362809号〔これらの文献におけるすべての反射防止（ハレーション防止）組成物とその使用を記載する部分は本発明の一部として参照される〕参照。このようなBARCおよびTARC層も一般に反射防止層または反射防止組成物として文献に記載されている。典型的には、このような反射防止組成物は、放射線吸収成分、または発色団、ポリマーバインダーおよび1またはそれ以上の架橋剤を含む。たとえば、公知の反射防止組成物は典型的にはフリーのヒドロキシル基を有しないエポキシフェノールバインダー、または酸基を実質的に有しないアクリレートバインダーを含んでいた。

【0009】基体のトポグラフィー（topography）におけるバリエーションも解像度を制約する反射の問題を生じる。基体上のイメージは衝突放射線（impinging radiation）を種々のコントロールされていない方向へ散乱または反射させることがあり、フォトレジストの現像の均一性に影響を及ぼす。基体のトポグラフィーはより複雑な回路を設計しようとするとさらに複雑になり、反射された放射線の効果はさらに重大になる。例えば、多くのマイクロエレクトロニクス基体上で用いられる金属インターコネクはそのトポグラフィーと高反射性領域のために特に問題である。

【0010】基体のトポグラフィーにおけるバリエーションに起因する課題の1つの解決法は、フォトレジストを表面上に同じ高さで配置する方法であり、この方法は、米国特許第4557797号（Fuller et al.）に開示されている。該方法は、ポリ（メチルメタアクリレート）（PMMA）の比較的厚い下層を有する多層構造物を使用して、平坦な表面、反射防止コーティングである薄い中間層、およびフォトレジスト物質である薄い上層を提供する。しかし、この系は、結果として、除去されなければならない厚いポリマー層を形成する。そのような層は典型的には、化学機械研磨（CMP）、エッチングおよびウエットケミカル法をはじめとする様々な方法によって除去される。そのような除去プロセスによる追加の時間およびコストのために、ポリマー層は、その後の除去を助けるため、できるだけ薄いこ

とが望まれる。

【0011】基体のトポグラフィーにおけるバリエーションに伴う課題の他の解決法は、Adams et al.、Planarizing AR for DUV Lithography、Microlithography 1999: Advances in Resist Technology and Processing XVI、Proceedings of SPIE vol. 3678、part 2、pp849-856、1999に開示されている。これは、反射防止層と基体との間に別個の平坦化層を配置する必要性を低減させる、平坦化反射防止コーティングの使用を開示する。

【0012】誘電体層上へのフォトレジスト層の使用は、しばしばフォトレジスト層の「ポイズニング」をもたらす。これは誘電体層が物理または化学蒸着（P/CVD）により適用されたときに特に問題となる。そのようなポイズニングの理論は完全には理解されていないが、そのような誘電体層は顕著なフォトスピードシフト（photospeed shift）、リフティング、プロファイルの劣化、またはすでにパターン付けられているアパーチャー領域、たとえばデュアルダマシンプロセスにおけるトレンチデリライニエーション（trench delineation）の間のピア領域、における完全な溶解の禁止を起こす場合がある。そのようなポイズニングは、ディープUV（DUV）フォトレジストのような、ポジ型フォトレジストが使用された際に特に問題である。BARCはフォトレジスト層に対して有効な化学的バリアを提供するが、そのようなBARCは誘電体層によるそのようなポイズニングに対してバリア層を提供するのに十分に効果的ではなかった。

【0013】したがって、誘電体層によるフォトレジストのポイズニング効果に対する効果的なバリアを提供すること、特に平坦化された表面を提供するバリア層に対する必要性が存在する。

【0014】本発明は誘電体層によるフォトレジスト層のコンタミネーションまたはポイズニング効果を、減少ないし消滅させることが見いだされた。本発明の組成物が実質的に局部的に平坦な表面を形成することも見いだされた。さらに、本発明は定在波効果、ポーイング（bowing）、表面腐食、およびフットイング（footing）を、実質的に減少ないし消滅させることが見いだされた。

【0015】第1の態様において、本発明は1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含むバリア組成物であって、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する組成物を提供する。

【0016】第2の態様において、本発明は、誘電体基体上にバリア層を提供する方法であって、1以上の架橋



可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含むバリア組成物であって、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する組成物を、誘電体基体の表面上に配置する工程を含む、方法を提供する。

【0017】第3の態様において、本発明は、誘電体層とその上に配置されたバリア層を有するデバイスであって、該バリア層が、重合単位として1以上の架橋可能なポリマー、および1以上の架橋剤を有し、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する、1以上の架橋されたポリマーを含む、デバイスを提供する。

【0018】第4の態様において、本発明は、誘電体層とフォトレジスト層の間にバリア層を配置することを含む、フォトレジスト層のコンタミネーションを減少させる方法であって、該バリア層が、重合単位として1以上の架橋可能なポリマー、および1以上の架橋剤を有し、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する、1以上の架橋されたポリマーを含む、方法を提供する。

【0019】第5の態様において、本発明は、a) 基体の上に誘電体層を提供する工程、

b) 1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含み、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア組成物を、誘電体層の表面上に配置する工程、

c) 少なくとも部分的にバリア組成物を硬化するに十分な温度に基体を加熱し、バリア層を形成する工程、を含む、電子デバイスの製造方法を提供する。

【0020】第6の態様において、本発明は、a) 基体の上に誘電体層を提供する工程、

b) 1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含み、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア組成物を、誘電体層の表面上に配置する工程、

c) 少なくとも部分的にバリア組成物を硬化するに十分な温度に基体を加熱し、バリア層を形成する工程、

d) バリア層の表面に反射防止コーティングを配置する工程、

e) 反射防止コーティングの表面にフォトレジスト層を配置する工程、

を含む、電子デバイスの製造方法を提供する。

【0021】本明細書を通じて使用されるものとして、他に特に示されない限りは、次の略語は次の意味を有する：°C＝摂氏温度；g＝グラム；cm＝センチメートル；Å＝オングストローム；rpm＝1分間あたりの回転数；%wt＝重量パーセント；mol%＝モル%；mJ＝ミリジュール；cm<sup>2</sup>＝平方センチメートル；L＝

リットル；mL＝ミリリットル。用語「ポリマー」とは、ダイマー、トリマー、テトラマー、オリゴマー、ホモポリマー、コポリマー等を意味する。用語「モノマー」とは、重合されることができる、任意のエチレン性またはアセチレン性不飽和化合物をいう。用語「(メタ)アクリル」とは、アクリルおよびメタアクリルの両方を含み、さらに用語「(メタ)アクリレート」とは、アクリレートおよびメタアクリレートの両方を含む。同様に、用語「(メタ)アクリルアミド」とは、アクリルアミドおよびメタアクリルアミドの両方をいう。「アルキル」は直鎖、分岐鎖および環式アルキル基を含む。

「クロスリンカー」または「架橋剤」は、本明細書においては交換可能なものとして使用される。「アパーチャ」とは、ビア、トレンチおよびこれらの組み合わせをいう。「フューチャー(feature)」とは、アパーチャをはじめとした種々のジオメトリーをいう。特に他に示されていない限りは、全ての量は重量パーセントであり、全ての比率は重量比である。全ての数値範囲は境界値を含み、組み合わせ可能である。

【0022】本発明は誘電体層、特にPVDまたはCVDされた誘電体層とバリア層を有する基体を提供することに関する。本発明はさらに誘電体層によるフォトレジストまたは反射防止コーティング層のポイズニングまたはコンタミネーションを減少ないし消滅させることに関する。本発明は特に、フォトレジスト、反射防止コーティングまたは両方が誘電体層基体に適用された、電子デバイスの製造方法に関する。

【0023】本発明の組成物は、1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含むバリア組成物であって、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア層組成物として有用である。「酸性部位」とは、架橋可能なポリマー、架橋剤またはその両方に存在する1以上の酸性基を言う。酸性部位は、少なくとも部分的に、好ましくは実質的に、より好ましくは全くブロッキング基を含まない。「ブロッキング基を含まない」とは、エーテルまたはエステルのような、官能化されまたは反応されてブロックされた酸性基を形成していない酸性部位を言う。「実質的にブロッキング基を含まない」とは、酸性部位の50%以上が、官能化されまたは反応されてブロックされた酸性基を形成していない酸性部位を言う。好ましくは、酸性部位の30%以上、より好ましくは20%以上が、官能化されられてブロックされた酸性基を形成していない。そのような酸性部位としては、カルボン酸、スルホン酸、ホスホン酸、たとえば芳香族ヒドロキシル化合物のようなヒドロキシル化合物、酸無水物などがあげられるが、これらに限定されるものではない。酸性部位が芳香族ヒドロキシル化合物を含むことが好ましい。

【0024】架橋可能なポリマーが重合単位として、1

以上の酸性部位を有するモノマーを含むことが好ましく、1以上の芳香族ヒドロキシル含有モノマーを含むことがより好ましい。そのような架橋可能なポリマーにおいては、酸性部位を有するモノマーは典型的には約1から約99モル%、好ましくは少なくとも約3モル%、より好ましくは少なくとも約5モル%、さらにより好ましくは少なくとも約10モル%の量で存在する。特に好適な架橋可能なポリマーとしては、重合単位として少なくとも約20、30、40、50、60、70、80、および90モル%の酸性部位を有するモノマーを含むものがあげられる。

【0025】本発明において有用な、架橋可能なポリマーおよび架橋剤は、他の官能基を含むこともできる。好適な他の官能基としては、エステル基、ハロゲン、シアノ、(C<sub>1</sub>-C<sub>6</sub>)アルコキシなどがあげられるが、これらに限定されるものではない。そのようなポリマーおよび架橋剤は、1よりも多い酸性部位、たとえば1よりも多い芳香族ヒドロキシル基、または芳香族ヒドロキシル基とカルボン酸基との組み合わせを含むこともできる。

【0026】典型的には、架橋可能なポリマーは約8000以下、好ましくは約5000以下、より好ましくは約3000以下の重量平均分子量を有する。架橋可能なポリマーが、少なくとも約300、好ましくは少なくとも約400、より好ましくは少なくとも約500の重量平均分子量を有することが好ましい。すなわち、特に有用な重量平均分子量の範囲は、約300から約8000、より好ましくは約300から約5000である。

【0027】本発明の架橋可能なポリマーは小さな分子量と広い分子量分布を有する。本発明の分子量分布はポリマーの多分散度、すなわち重量平均分子量と数平均分子量との比率(M<sub>w</sub>/M<sub>n</sub>)として特性付けられる。本発明のポリマーは典型的には、少なくとも1.5、好ましくは少なくとも1.8、より好ましくは少なくとも2.0、さらにより好ましくは少なくとも2.5、さらにより好ましくは少なくとも3.0、最も好ましくは少なくとも3.5のM<sub>w</sub>/M<sub>n</sub>、すなわち多分散度を有する。そのような架橋可能なポリマーの典型的な多分散度は1.5から4、好ましくは1.8から4、より好ましくは2から4の範囲である。

【0028】好適な架橋可能なポリマーとしては、芳香族アルデヒド縮合物、およびポリ(ビニルフェノール)のような、1以上のヒドロキシル基含有モノマーの重合単位を有する任意のポリマーがあげられるが、これらに限定されるものではない。本発明において有用な芳香族アルデヒド縮合物としては、フェノールノボラック樹脂が挙げられるがこれに限定されるものではない。そのようなノボラック樹脂は、典型的には、フェノールのアルデヒドとの縮合によって調製され、さらに該ノボラック樹脂は公知であり、Kirk Othmer Enc

cyclopedia of Chemical Technology、15巻、176~208ページ、1968を含む多くの刊行物に開示されており、該刊行物におけるそのような樹脂を教示する記載は本明細書の一部として参照される。フェノールはそれ自体が、そのようなフェノール樹脂の形成のために一般的に使用されるフェノールであるが、例えば、特に限定されるものではないが、レゾルシノール；ナフトール、クレゾール、キシレノールおよびp-tert-ブチルフェノールをはじめとするアルキル置換フェノール；並びにp-フェニルフェノールおよび4,4'-イソプロピリデンジフェノールをはじめとするビスフェノールのような、他のヒドロキシ置換芳香族化合物も同様に好適である。好ましいフェノール類としてはクレゾールが挙げられ、より好ましくは、m-クレゾール、m-およびp-クレゾールの混合物、2,5-キシレノール、並びにこれらの混合物が挙げられる。ヒドロキシ置換芳香族化合物の混合物は、本発明において有利に使用されることができる。

【0029】使用されるアルデヒドは典型的にはホルムアルデヒドであるが、これらに限定されるものではないが、たとえばアセトアルデヒド、フルフルアルデヒド、および芳香族アルデヒドのような他のアルデヒドを使用することもできる。好ましい芳香族アルデヒドは、ヒドロキシル基がカルボニル基のオルト位にあるものである。最も好ましい芳香族アルデヒドはサリチルアルデヒド、ベンズアルデヒド、およびそれらの混合物である。本発明の目的のために好適な他の芳香族アルデヒドとしては、2-クロロベンズアルデヒド、3-ヒドロキシルベンズアルデヒド、4-ヒドロキシルベンズアルデヒド、2-メトキシベンズアルデヒド、3-ニトロベンズアルデヒド、などがあげられる。アルデヒドの混合物も本発明において有用に使用することができる。芳香族アルデヒドがホルムアルデヒド、またはホルムアルデヒド前駆体、たとえばパラホルムアルデヒドと混合される場合には、芳香族アルデヒドは好ましくはホルムアルデヒドよりもモル過剰で存在し、より好ましくはアルデヒド混合物の少なくとも90重量%で存在する。

【0030】典型的には、フェノールノボラック樹脂はフェノールの縮合、すなわち酸の存在下にヒドロキシル置換された芳香族化合物とアルデヒドから形成される。アルデヒドのモル濃度はフェノールのモル濃度よりも若干少ないことができるが、等量であることができ、架橋した樹脂を形成しないでフェノールの若干過剰であることもできる。この観点から、フェノールとアルデヒドとの比は、約1.1対1.0から1.0対1.1の間で変化することができる。たとえば、米国特許第5939511号(Zampini)参照。一般に、本発明において架橋可能なポリマーとして有用な、そのような芳香族アルデヒド縮合物の多分散度は、少なくとも約2.5、好ましくは少なくとも約3.0、より好ましく

は少なくとも約3.5である。

【0031】任意のヒドロキシル基含有エチレン性またはアセチレン性不飽和化合物が本発明においてヒドロキシル基含有モノマーとして有用である。そのようなヒドロキシル基含有モノマーは、脂肪族または芳香族であることができ、好ましくは芳香族である。好適なヒドロキシル基含有モノマーとしては、フェノール、クレゾール、レゾルシノール、ピロガロール、メチロールフェノール、メチロールクレゾール、メチロールレゾルシノール、メチロールピロガロール、ヒドロキシエチルフェノール、ヒドロキシプロピルフェノール、ヒドロキシエチルクレゾール、ビニルフェノール、ビニルクレゾール、ビニルメトキシフェノール、ヒドロキシエチル(メタ)アクリレート、2-ヒドロキシプロピル(メタ)アクリレート、3-ヒドロキシプロピル(メタ)アクリレート、ヒドロキシシクロヘキシル(メタ)アクリレート、ヒドロキシフェニル(メタ)アクリレート、ジエチレングリコール(メタ)アクリレート、ビス(ヒドロキシエチル)イタコネート、ビス(ヒドロキシエチル)シトラコネート、ビス(ヒドロキシエチル)フマレート、ヒドロキシエチルイタコネート、アリルフェノール、アリルメトキシフェノール、アリルアルコール、ビニルアルコールなどがあげられるが、これらに限定されるものではない。

【0032】本発明の架橋可能なポリマーが、重合単位として1以上の芳香族化合物を、たとえば少なくとも約3モル%、好ましくは少なくとも約5モル%、より好ましくは少なくとも約10モル%含むことが好ましい。好ましい芳香族化合物としては、フェノール性化合物、クレゾール化合物、レゾルシノール化合物、キシレノール化合物等があげられるが、これらに限定されるものではない。特に有用な架橋可能なポリマーとしては、重合単位として少なくとも約20モル%の芳香族化合物を含むものがあげられる。架橋可能なポリマーが1以上の芳香族-アルデヒド縮合物を含むことがさらに好ましい。

【0033】特に有用な架橋可能なポリマーは、1以上の芳香族-アルデヒド縮合物および1以上の他のポリマー、たとえば(メタ)アクリレートポリマーを含むものであって、芳香族-アルデヒド縮合物の $M_w/M_n$ の値が少なくとも2.5、好ましくは少なくとも3.0であるものである。たとえば(メタ)アクリレートポリマーのような、非芳香族ポリマーを芳香族-アルデヒド縮合物とともに含む利点は、バリア組成物のエッチング速度が増加される場合のあることである。本発明の架橋可能なポリマーが実質的にシルフェニレン部位を含まないことがさらに好ましく、より好ましくはシルフェニレン部位を含まない。

【0034】本発明の架橋可能なポリマーを調製するために有用なモノマーとしては、(メタ)アクリル酸、(メタ)アクリルアミド、アルキル(メタ)アクリレ-

ト、アルケニル(メタ)アクリレート、芳香族(メタ)アクリレート、ビニル芳香族モノマー、窒素含有化合物およびそのチオアナログ、置換されたエチレンモノマーなどがあげられるが、これらに限定されるものではない。本発明において有用な特に好ましい架橋可能なポリマーとしては、芳香族-アルデヒド縮合物の混合物があげられ、特にノボラック樹脂と、1以上のポリ(メタ)アクリル酸)、ポリ(メタ)アクリルアミド)、ポリ(アルキル(メタ)アクリレート)、ポリ(アルケニル(メタ)アクリレート)、ポリ(芳香族(メタ)アクリレート)、ポリ(ビニル芳香族)との混合物である。

【0035】典型的には、本発明において有用なアルキル(メタ)アクリレートは、(C<sub>1</sub>-C<sub>24</sub>)アルキル(メタ)アクリレートである。好適なアルキル(メタ)アクリレートとしては、「ローカット(low cut)」アルキル(メタ)アクリレート、「ミッドカット(mid cut)」アルキル(メタ)アクリレートおよび「ハイカット(high cut)」アルキル(メタ)アクリレートが挙げられるが、これらに限定されるものではない。「ローカット」アルキル(メタ)アクリレートは、典型的には、アルキル基が1~6個の炭素原子を有するものである。好適なローカットアルキル(メタ)アクリレートとしては、メチルメタアクリレート(MMA)、メチルアクリレート、エチルアクリレート、プロピルメタアクリレート、ブチルメタアクリレート(BMA)、ブチルアクリレート(BA)、イソブチルメタアクリレート(IBMA)、ヘキシルメタアクリレート、シクロヘキシルメタアクリレート、シクロヘキシルアクリレート、およびこれらの混合物が挙げられるがこれらに限定されるものではない。

【0036】「ミッドカット」アルキル(メタ)アクリレートは、典型的には、アルキル基が7~15個の炭素原子を有するものである。好適なミッドカットアルキル(メタ)アクリレートとしては、2-エチルヘキシルアクリレート(EHA)、2-エチルヘキシルメタアクリレート、オクチルメタアクリレート、デシルメタアクリレート、イソデシルメタアクリレート(IDMA、分岐(C10)アルキル異性体混合物をベースとする)、ウンデシルメタアクリレート、ドデシルメタアクリレート(ラウリルメタアクリレートとしても知られる)、トリデシルメタアクリレート、テトラデシルメタアクリレート(ミリスチルメタアクリレートとしても知られる)、ペンタデシルメタアクリレート、およびこれらの混合物が挙げられるがこれらに限定されるものではない。特に有用な混合物としては、ドデシル-ペンタデシルメタアクリレート(DPMA)、直鎖および分岐鎖のドデシル、トリデシル、テトラデシルおよびペンタデシルメタアクリレートの混合物; およびラウリル-ミリスチルメタアクリレート(LMA)が挙げられる。

【0037】「ハイカット」アルキル(メタ)アクリレ-

ートは、典型的には、アルキル基が16～24個の炭素原子を有するものである。好適なハイカットアルキル(メタ)アクリレートとしては、ヘキサデシルメタアクリレート、ヘプタデシルメタアクリレート、オクタデシルメタアクリレート、ノナデシルメタアクリレート、コシルメタアクリレート、エイコシルメタアクリレート、およびこれらの混合物が挙げられるがこれらに限定されるものではない。ハイカットアルキル(メタ)アクリレートの特に有用な混合物としては、ヘキサデシル、オクタデシル、コシルおよびエイコシルメタアクリレートの混合物であるセチルーエイコシルメタアクリレート(CEMA)；並びにヘキサデシルおよびオクタデシルメタアクリレートの混合物であるセチルステアリルメタアクリレート(SMA)が挙げられるがこれらに限定されるものではない。

【0038】上述のミッドカットおよびハイカットアルキル(メタ)アクリレートモノマーは、概して、試薬グレードの長鎖脂肪族アルコールを用いた標準的なエステル化方法によって調製され、これら商業的に入手可能なアルコールは、アルキル基が炭素原子を10～15個または16～20個有する、様々な鎖長のアルコールの混合物である。これらのアルコールの例としては、Vista Chemical companyからの、様々なチーグラ触媒化(Ziegler catalyzed)ALFOLアルコール、すなわち、ALFOL1618およびALFOL1620、Shell Chemical Companyからの様々なチーグラ触媒化NEODOLアルコール、すなわち、NEODOL25L、並びにProctor & Gamble's社のTA-1618およびCO-1270のような天然物由来のアルコールが挙げられる。よって、本発明の目的のためには、アルキル(メタ)アクリレートは、命名された個々のアルキル(メタ)アクリレート製品を含むだけでなく、命名された特定のアルキル(メタ)アクリレートを主として含む、アルキル(メタ)アクリレートの混合物も含むものと意図される。

【0039】本発明において有用なアルキル(メタ)アクリレートモノマーは、単独のモノマーであるか、またはアルキル部分の炭素原子の数が異なっている混合物であることができる。また、本発明において有用な、(メタ)アクリルアミドおよびアルキル(メタ)アクリレートモノマーは任意に置換されることができる。好適な任意の置換(メタ)アクリルアミドおよびアルキル(メタ)アクリレートモノマーとしては、ヒドロキシ(C<sub>2</sub>-C<sub>6</sub>)アルキル(メタ)アクリレート、ジアルキルアミノ(C<sub>2</sub>-C<sub>6</sub>)-アルキル(メタ)アクリレート、ジアルキルアミノ(C<sub>2</sub>-C<sub>6</sub>)アルキル(メタ)アクリルアミドが挙げられるがこれらに限定されるものではない。特に有用な置換アルキル(メタ)アクリレートモノマーは、アルキル基に1以上のヒドロキシル基を有す

るものであり、特に、ヒドロキシル基がアルキル基においてβ-位(2-位)にあるものである。置換アルキル基が分岐鎖または直鎖の(C<sub>2</sub>-C<sub>6</sub>)アルキルであるヒドロキシアリル(メタ)アクリレートモノマーが好ましい。好適なヒドロキシアリル(メタ)アクリレートモノマーとしては、2-ヒドロキシエチルメタアクリレート(HEMA)、2-ヒドロキシエチルアクリレート(HEA)、2-ヒドロキシプロピルメタアクリレート、1-メチル-2-ヒドロキシエチルメタアクリレート、2-ヒドロキシプロピルアクリレート、1-メチル-2-ヒドロキシエチルアクリレート、2-ヒドロキシブチルメタアクリレート、2-ヒドロキシブチルアクリレート、およびこれらの混合物が挙げられるがこれらに限定されるものではない。好適なヒドロキシアリル(メタ)アクリレートモノマーはHEMA、1-メチル-2-ヒドロキシエチルメタアクリレート、2-ヒドロキシプロピルメタアクリレート、およびこれらの混合物である。後者の2つのモノマーの混合物は、一般に、「ヒドロキシプロピルメタアクリレート」または「HPMA」と呼ばれる。

【0040】本発明において有用な、他の置換された(メタ)アクリレートと(メタ)アクリルアミドモノマーは、アルキル基にジアルキルアミノ基またはジアルキルアミノアルキル基を有するものである。そのような置換された(メタ)アクリレートと(メタ)アクリルアミドの例としては、ジメチルアミノエチルメタアクリレート、ジメチルアミノエチルアクリレート、N,N-ジメチルアミノエチルメタアクリルアミド、N,N-ジメチルアミノプロピルメタアクリルアミド、N,N-ジメチルアミノブチルメタアクリルアミド、N,N-ジエチルアミノエチルメタアクリルアミド、N,N-ジエチルアミノプロピルメタアクリルアミド、N,N-ジエチルアミノブチルメタアクリルアミド、N-(1,1-ジメチル-3-オキソブチル)アクリルアミド、N-(1,3-ジフェニル-1-エチル-3-オキソブチル)アクリルアミド、N-(1-メチル-1-フェニル-3-オキソブチル)メタアクリルアミド、および2-ヒドロキシエチルアクリルアミド、アミノエチルエチレンウレアのN-メタアクリルアミド、N-メタアクリルオキシエチルモルホリン、ジメチルアミノプロピルアミンのN-マレイミド、並びにこれらの混合物が挙げられるがこれらに限定されるものではない。

【0041】本発明に有用な他の置換(メタ)アクリレートモノマーは、γ-プロピトリ(C<sub>1</sub>-C<sub>6</sub>)アルコキシシリル(メタ)アクリレート、γ-プロピトリ(C<sub>1</sub>-C<sub>6</sub>)アルキルシリル(メタ)アクリレート、γ-プロピルジ(C<sub>1</sub>-C<sub>6</sub>)アルコキシ(C<sub>1</sub>-C<sub>6</sub>)アルキルシリル(メタ)アクリレート、γ-プロピルジ(C<sub>1</sub>-C<sub>6</sub>)アルキル(C<sub>1</sub>-C<sub>6</sub>)アルコキシシリル(メタ)アクリレート、ビニトリ(C<sub>1</sub>-C

6) アルコキシシリル(メタ)アクリレート、ビニルジ(C<sub>1</sub>-C<sub>6</sub>)アルコキシ(C<sub>1</sub>-C<sub>6</sub>)アルキルシリル(メタ)アクリレート、ビニル(C<sub>1</sub>-C<sub>6</sub>)アルコキシジ(C<sub>1</sub>-C<sub>6</sub>)アルキルシリル(メタ)アクリレート、ビニルトリ(C<sub>1</sub>-C<sub>6</sub>)アルキルシリル(メタ)アクリレート、及びこれらの混合物等のシリコン含有モノマーである。

【0042】本発明の不飽和モノマーとして有用なビニル芳香族モノマーには、スチレン(「STY」)、 $\alpha$ -メチルスチレン、ビニルトルエン、 $p$ -メチルスチレン、エチルビニルベンゼン、ビニルナフタレン、ビニルキシレン、及びこれらの混合物が含まれるが、これらに限定されない。ビニル芳香族モノマーには、また、ハロゲン化誘導体、即ち、フッ素、塩素又は臭素等の1以上のハロゲン基を含む誘導体；及びニトロ、シアノ、(C<sub>1</sub>-C<sub>10</sub>)アルコキシ、ハロ(C<sub>1</sub>-C<sub>10</sub>)アルキル、カルブ(C<sub>1</sub>-C<sub>10</sub>)アルコキシ、カルボキシ、アミノ、(C<sub>1</sub>-C<sub>10</sub>)アルキルアミノ誘導体等のそれらの相当する置換対応物が含まれる。

【0043】本発明の不飽和モノマーとして有用な窒素含有化合物及びチオアナログには、2-ビニルピリジン又は4-ビニルピリジン等のビニルピリジン；2-メチル-5-ビニルピリジン、2-エチル-5-ビニルピリジン、3-メチル-5-ビニルピリジン、2, 3-ジメチル-5-ビニルピリジン、及び2-メチル-3-エチル-5-ビニルピリジン等の低級アルキル(C<sub>1</sub>-C<sub>8</sub>)置換N-ビニルピリジン；メチル置換キノリン及びイソキノリン；N-ビニルカプロラクタム；N-ビニルブチロラクタム；N-ビニルピロリドン；ビニルイミダゾール；N-ビニルカルバゾール；N-ビニルスクシンイミド；(メタ)アクリロニトリル； $o$ -,  $m$ -, 又は  $p$ -アミノスチレン；マレイミド；N-ビニルオキサゾリドン；N, N-ジメチルアミノエチル-ビニルエーテル；エチル-2-シアノアクリレート；ビニルアセトニトリル；N-ビニルフタルイミド；N-ビニルチオ-ピロリドン、3-メチル-1-ビニル-ピロリドン、4-メチル-1-ビニル-ピロリドン、5-メチル-1-ビニル-ピロリドン、3-エチル-1-ビニル-ピロリドン、3-ブチル-1-ビニル-ピロリドン、3, 3-ジメチル-1-ビニル-ピロリドン、4, 5-ジメチル-1-ビニル-ピロリドン、5, 5-ジメチル-1-ビニル-ピロリドン、3, 3, 5-トリメチル-1-ビニル-ピロリドン、4-エチル-1-ビニル-ピロリドン、5-メチル-5-エチル-1-ビニル-ピロリドン及び3, 4, 5-トリメチル-1-ビニル-ピロリドン等のN-ビニルピロリドン；ビニルピロール；ビニルアニリン；及びビニルピペリジンが含まれるが、これらに限定されない。

【0044】本発明において不飽和モノマーとして有用な置換エチレンモノマーには、アリルモノマー、酢酸ビ

ニル、ビニルホルムアミド、塩化ビニル、フッ化ビニル、臭化ビニル、塩化ビニリデン、フッ化ビニリデン、および臭化ビニリデン酸が含まれるが、これらに限定されない。架橋可能なポリマーは本発明の組成物中に、幅広い範囲の量で存在する。典型的には、架橋可能なポリマーは固形分の約40から約85%、好ましくは約60から約85%の量で存在する。

【0045】本発明において有用な架橋剤は、架橋可能なポリマーと酸触媒架橋を行うことのできる任意の物質である。典型的には、本発明の架橋剤は約120ダルトンまたはそれ以上の分子量を有する。架橋剤が約75℃から約250℃の温度で架橋反応を行うことが好ましい。好適な架橋剤には、ジ-、トリ-、テトラ-、又はより高位の多官能性エチレン不飽和モノマーが含まれる。本発明に有用な架橋剤の例としては、トリビニルベンゼン、ジビニルトルエン、ジビニルピリジン、ジビニルナフタレン及びジビニルキシレン；及び例えば、エチレングリコールジアクリレート、トリメチロールプロパントリアクリレート、ジエチレングリコールジビニルエーテル、トリビニルシクロヘキサン、アリルメタクリレート(「ALMA」)、エチレングリコールジメタクリレート(「EGDMA」)、ジエチレングリコールジメタクリレート(「DEGDMA」)、プロピレングリコールジメタクリレート、プロピレングリコールジアクリレート、トリメチロールプロパントリメタクリレート(「TMPTMA」)、ジビニルベンゼン(「DVB」)、グリシジルメタクリレート、2, 2-ジメチルプロパン1, 3-ジアクリレート、1, 3-ブチレングリコールジアクリレート、1, 3-ブチレングリコールジメタクリレート、1, 4-ブタンジオールジアクリレート、ジエチレングリコールジアクリレート、ジエチレングリコールジメタクリレート、1, 6-ヘキサジオールジアクリレート、1, 6-ヘキサジオールジメタクリレート、トリプロピレングリコールジアクリレート、トリエチレングリコールジメタクリレート、テトラエチレングリコールジアクリレート、ポリエチレングリコール200ジアクリレート、テトラエチレングリコールジメタクリレート、ポリエチレングリコールジメタクリレート、エトキシ化ビスフェノールAジアクリレート、エトキシ化ビスフェノールAジメタクリレート、ポリエチレングリコール600ジメタクリレート、ポリ(ブタンジオール)ジアクリレート、ペンタエリスリトールトリアクリレート、トリメチロールプロパントリエトキシトリアクリレート、グリセリルプロポキシトリアクリレート、ペンタエリスリトールテトラアクリレート、ペンタエリスリトールテトラメタクリレート、ジペンタエリスリトールモノヒドロキシペンタアクリレート、ジビニルシラン、トリビニルシラン、ジメチルジビニルシラン、ジビニルメチルシラン、メチルトリビニルシラン、ジフェニルジビニルシラン、ジビニルフェニルシラン、トリ

ビニルフェニルシラン、ジビニルメチルフェニルシラン、テトラビニルシラン、ジメチルビニルジシロキサン、ポリ（メチルビニルシロキサン）、ポリ（ビニルヒドロシロキサン）、ポリ（フェニルビニルシロキサン）、テトラメトキシグリコールウリルおよびテトラブトキシグリコールウリルのようなテトラ（C<sub>1</sub>—C<sub>8</sub>）アルコキシグリコールウリル、及びこれらの混合物があげられるが、これらに限定されない。

【0046】本発明の架橋剤は本発明の組成物において幅広い範囲の量で存在する。典型的には、架橋剤は固形分の約1から約30%、好ましくは約10から約25%、より好ましくは約15から約25%の量で存在する。本発明において有用な酸触媒は、本発明のバリア層組成物の架橋反応を触媒することのできる任意のものであり、フリー酸（free acid）および酸生成剤（acid generator）があげられる。フリー酸の例としては、メタンスルホン酸、エタンスルホン酸、プロピルスルホン酸、フェニルスルホン酸、トルエンスルホン酸、ドデシルベンゼンスルホン酸、およびトリフルオロメチルスルホン酸があげられるが、これらに限定されるものではない。

【0047】酸生成剤としては、熱酸生成剤（TAG）およびフォト酸生成剤（PAG）、およびそれらの混合物があげられる。任意の熱酸生成剤およびフォト酸生成剤が本発明において有用である。熱酸生成剤は、熱処理により酸を遊離する任意の化合物である。好適な熱酸生成剤としては、2, 4, 4, 6-テトラブromoシクロヘキサジエノン、ベンゾイントシレート、2-ニトロベンジルトシレート及び他の有機スルホン酸のアルキルエステル、スルホン酸のアミン塩、たとえばドデシルベンゼンスルホン酸のアミン塩があげられるが、これらに限定されるものではない。活性化、すなわち熱への暴露によりスルホン酸を発生するものが一般に好ましい。フォト酸生成剤は、光分解により酸を遊離する化合物である。好適なフォト酸生成剤としては、オニウム塩およびハロゲン化非イオン性フォト酸生成剤、たとえば1, 1-ビス（p-クロロフェニル）-2, 2, 2-トリクロロエタンおよび、ペルフルオロオクチルスルホン酸のようなフルオロアルキルスルホン酸があげられるが、これらに限定されるものではない。

【0048】酸触媒は、典型的には本発明の組成物中に、所望の架橋反応を触媒するのに十分な量、たとえば固形分の約0.1から8%、好ましくは固形分の約0.5から約5%の量で存在する。酸触媒の組み合わせを使用することが、本発明においては好ましい。好適な組み合わせとしては、フリー酸とフォト酸生成剤、並びにフリー酸と熱酸生成剤があげられる。そのような酸触媒は一般に知られ、商業的に利用可能であり、さらに精製することなく使用することができる。

【0049】本発明の組成物は1以上の溶剤を含む。配

合物との適合性の任意の溶剤が適当である。低粘度の溶剤が好ましい。好適な溶媒としては、例えばプロピレングリコールメチルエーテルアセテート、2-ヘプタノン、乳酸エチル、または1以上のグリコールエーテル、例えば2-メトキシエチルエーテル（ジグリム）、エチレングリコールモノメチルエーテル、プロピレングリコールモノメチルエーテル；エーテル部位およびヒドロキシ部位の両方を有する溶剤、たとえばメトキシブタノール、エトキシブタノール、メトキシプロパノール、およびエトキシプロパノール；エステル、たとえばメチルセロソルブアセテート、エチルセロソルブアセテート、プロピレングリコールモノメチルエーテルアセテート、ジプロピレングリコールモノメチルエーテルアセテート、および他の溶剤、たとえば二塩基性エステル、プロピレンカルボネート、およびガンマーブチロラクトンなどがあげられるが、これらに限定されるものではない。本発明において有用な、特に好適な溶剤は比較高い沸点、すなわち少なくとも約170℃、好ましくは少なくとも約190℃の沸点を有する溶剤である。溶剤の混合物も本発明において有用に使用することができる。すなわち、本発明の溶剤は1以上の他の溶剤と混合することができる。そのような他の溶剤は高沸点または低沸点であることができる。2以上の溶剤が使用される場合には、少なくとも1つの溶剤が約75℃から約200℃の範囲の沸点を有することが好ましい。2以上の溶剤が使用される場合には、少なくとも1つの溶剤が約200未満の沸点を有し、少なくとも1つの他の溶剤が約200℃よりも高い沸点を有することが好ましい。

【0050】本発明の組成物は、任意に1以上の他の成分、これらに限定されるものではないが、たとえば可塑剤、界面活性剤、平滑剤、染料、発色団、顔料などを含むことができる。可塑剤は本発明の組成物に、組成物の特定の特性を改良するために加えることができる。好適な可塑剤としては、ジメチルアジペートおよびジメチルスクシネートのような二塩基性エステルがあげられるが、これらに限定されるものではない。可塑剤の混合物を本発明において使用することができる。典型的には、可塑剤は固形分の約0.5から約10%、好ましくは約1%から約5%の量で使用される。本発明において1以上の可塑剤が使用されることが好ましい。固形分の約50%までから約100%のような多量の可塑剤が、本発明において有用に使用されることは当業者に理解されるであろう。可塑剤は液体であることが好ましい。

【0051】任意の界面活性剤としては、非イオン性界面活性剤、カチオン性界面活性剤、およびそれらの混合物があげられるが、これらに限定されるものではない。特に好適な界面活性剤は、フッ素化界面活性剤、たとえば3Mカンパニーから販売されるものがあげられる。界面活性剤は典型的には約0.1から約1.0重量%の範囲で使用される。

【0052】本発明において有利なレベリング剤としては、Witcoからの商品名Silwet 7604として入手可能なものをはじめとする表面レベリング剤、または3M Companyから入手可能な界面活性剤FC430が挙げられる。そのようなレベリング剤の選択および量は当業者の能力の範囲内の事項である。典型的には、そのようなレベリング剤は、総固形分の約0.1から約2%の量で使用される。

【0053】本発明の組成物は反射防止コーティングとしても作用することができる。たとえば、架橋可能なポリマーおよび/または架橋剤が芳香族基を含む場合、そのような組成物は193nm放射線に対して反射防止組成物として使用することができる。別法として、染料または発色団をたとえば共重合または混合により本発明の組成物に加え、他の波長の放射線において有用な反射防止組成物を提供することができる。たとえば、架橋可能なポリマーおよび/または架橋剤に十分な発色団を含有させ、引き続き適用されるフォトレジスト層に使用される露光波長において、約0.3から約0.8の光学濃度を得ることができる。別法として、アントラセン化合物のような発色団を本発明の組成物に直接加えることができる。

【0054】溶剤中の乾燥成分の濃度、すなわち1以上の架橋可能なポリマー、1以上の酸触媒、および1以上の架橋剤の濃度は、塗布方法のような多くの要因に応じて変化する。一般に、本発明の組成物の固形分含量は、組成物の合計重量の約0.5から25重量%であり、好ましくは固形分含量は、組成物の合計重量の約2から20重量%である。本発明の組成物は、成分を任意の順番で組み合わせることにより調製される。

【0055】本発明の組成物は、電子デバイス、たとえば半導体、導体、集積回路、プリント基板などの製造において、基体、特に誘電体層基体の上のバリア層として有用である。本発明の組成物は、半導体の製造において使用されるウエハーのような半導体デバイスの製造において特に有用である。本発明の組成物は、例えばスピニングのような任意の種々の方法で基体に適用することができる。基体に適用する際、本発明の組成物は基体表面上に配置されたコーティングまたは層を提供する。たとえば半導体ウエハーに、組成物がスピニングにより適用された場合、得られるフィルムの厚さは、たとえば約200オングストローム未満から約1.5ミクロン、好ましくは約200オングストロームから約1.5ミクロンの範囲で制御することができる。典型的には、本発明のバリア組成物は、約600から約1600オングストローム、好ましくは約600から1200オングストロームの層で適用される。

【0056】すなわち、本発明は、誘電体基体上にバリア層を提供する方法であって、1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上

の溶剤を含むバリア組成物であって、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する組成物を、誘電体基体の表面上に配置する工程を含む方法を提供する。

【0057】本発明のバリア層は、任意の誘電体層、好ましくはPVDまたはCVD堆積された誘電体層、による、任意のフォトレジストまたは反射防止コーティングの汚染を減少ないしなくするために有利に使用される。好適な誘電体層としては、無機誘電体層、有機誘電体層、およびこれらの混合物があげられ、好ましくは無機誘電体層である。好適な無機誘電体層としては、シリカ、シルセスキオキサン(silsesquioxane)、部分的に縮合されたアルコキシシラン、有機的に改質されたシリケートなどのシリコン含有誘電体層があげられるが、これらに限定されるものではない。種々の有機誘電体物質も、本発明において使用することができる。

【0058】典型的には、本発明の組成物は約75から約250℃、好ましくは約90から約225℃に加熱することにより、少なくとも部分的に架橋される。「少なくとも部分的に架橋される」とは、バリア組成物の少なくとも約10%が架橋されることを言う。バリア組成物が実質的に架橋されることが好ましく、より好ましくは完全に架橋される。本発明の組成物は、組成物でコーティングされた基体を1工程または2工程バイクに供することにより硬化することができる。1工程バイクでは、少なくとも部分的に、好ましくは実質的に組成物を架橋するのに十分な温度および期間、本発明の組成物を加熱する。別法として、2工程バイクでは、組成物を架橋するには十分でないが、組成物をリフローさせて平滑性を改良する第1の温度に加熱し、ついで少なくとも部分的に、好ましくは実質的に組成物を架橋するのに十分な第2の温度および期間、本発明の組成物を加熱する。

【0059】一般に、本発明の組成物は約15から約360秒、好ましくは約15から約120秒、より好ましくは約30から約120秒、さらにより好ましくは約60秒、硬化される。具体的な硬化時間は、架橋剤の種類、架橋剤の量、酸触媒の量、加熱温度などにより変化することが、当業者に理解されるであろう。本発明は、さらに、誘電体層とその上に配置されるバリア層を有するデバイスであって、該バリア層が、重合単位として1以上の架橋可能なポリマー、および1以上の架橋剤を有し、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有する、1以上の架橋されたポリマーを含む、デバイスを提供する。そのようなデバイスにおいて、フォトレジスト層が、バリア層の上に配置されていることが好ましい。反射防止組成物がバリア層およびフォトレジスト層の間に配置されることがさらに好ましい。

【0060】電子デバイス、特に半導体ウエハーの製造

において、たとえば物理蒸着（PVD）または化学蒸着（CVD）により誘電体層がしばしば適用される。これらの誘電体層は引き続きエッチングおよびメタライゼーション工程のために、パターン付けられることが必要である。そのようなパターンニングはフォトレジストの使用により達成され、しばしば反射防止コーティングとともに使用される。フォトレジスト層を適用する前の本発明のバリア組成物の層の適用、好ましくは反射防止コーティングを適用する前の適用は、誘電体層によるフォトレジスト層のボイズニングまたはコンタミネーションを減少し、またはなくす。

【0061】フォトレジスト層のボイズニングまたはコンタミネーションは、フューチャーの解像度の減少により立証される。たとえば、図1は、バリア層を使用することなく形成された誘電体層中のコンタクトホール、走査電子顕微鏡（SEM）の断面写真である。コンタクトホールの底部における顕著なボーイングが、この図において明確に見られる。本発明のバリア層が使用された場合、フォトレジスト層のボイズニングまたはコンタミネーションは、ボーイングにより示されるように、大きく減少され、または解消される。図2は、600オングストロームの本発明のバリア層を使用して形成された誘電体層中のコンタクトホールの走査電子顕微鏡（SEM）の断面写真である。図1に比較して、コンタクトホールの底部におけるボーイングの量の減少が明確にみられる。本発明のバリア層がより厚くなると、そのようなボイズニングまたはコンタミネーションがさらに減少される。図3から5は、それぞれ1000オングストローム、1500オングストローム、および2000オングストロームの厚さのバリア層を使用して形成された誘電体層中のコンタクトホールの走査電子顕微鏡（SEM）の断面写真である。図2ないし5からわかるように、本発明のバリア層はフォトレジスト層のボイズニングまたはコンタミネーションを、ボーイングにより示されるように、顕著に減少させる。

【0062】本発明は、a) 基体の上に誘電体層を提供する工程、b) 1以上の架橋可能なポリマー、1以上の酸触媒、1以上の架橋剤、および1以上の溶剤を含み、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア組成物を、誘電体層の表面上に配置する工程、c) 少なくとも部分的にバリア組成物を硬化するに十分な温度に基体を加熱し、バリア層を形成する工程、を含む、電子デバイスの製造方法を提供する。典型的には、フォトレジスト層はバリア層の表面上に配置される。反射防止コーティングがバリア層の表面とフォトレジスト層の表面との間に配置されるのが好ましい。フォトレジスト層がポジ型フォトレジストを含むことがさらに好ましい。

【0063】本発明は、a) 基体の上に誘電体層を提供する工程、b) 1以上の架橋可能なポリマー、1以上の

酸触媒、1以上の架橋剤、および1以上の溶剤を含み、架橋可能なポリマーと架橋剤の少なくとも1つが1以上の酸性部位を有するバリア組成物を、誘電体層の表面上に配置する工程、c) 少なくとも部分的にバリア組成物を硬化するに十分な温度に基体を加熱し、バリア層を形成する工程、d) バリア層の表面に反射防止コーティングを配置する工程、e) 反射防止コーティングの表面にフォトレジスト層を配置する工程、を含む、電子デバイスの製造方法を提供する。

【0064】本発明のバリア層が、反射防止コーティングを用いずに使用される場合、バリア層が少なくとも約1000オングストローム、より好ましくは少なくとも約1200オングストローム、さらにより好ましくは少なくとも約1500オングストロームの厚さを有することが好ましい。反射防止コーティングがバリア層とフォトレジスト層との間に配置される場合、バリア層が少なくとも約400オングストローム、より好ましくは少なくとも約600オングストロームの厚さを有することが好ましい。バリアの厚さの典型的な範囲は、約400から約2500オングストローム、好ましくは約600から約2000オングストローム、より好ましくは約800から1500オングストロームである。一般に、反射防止コーティングは、約200から約2000オングストローム、好ましくは約400から約1600オングストロームの厚さを有する。フォトレジスト層は、一般に、約200から約10000オングストローム、好ましくは約500から約7500オングストロームの厚さを有する。

【0065】本発明の組成物の利点は、それらがフォトレジストおよびスピナーオンされた誘電体とスピナー適合性（spin bowl compatible）であることである。本発明は半導体製造に関して説明されたが、本発明は幅広い用途において使用できる。以下の例は本発明の種々の態様を例示するものであり、本発明の範囲を何ら制限するものではない。

#### 【0066】実施例1

バリア層組成物が、以下を組み合わせることにより調製された：メタクレゾール-パラクレゾール-2、5-ジメトキシフェノールノボラックポリマー（プロピレングリコールモノメチルエーテルアセテート（PGMEA）中の固形分30%の溶液、301.268g、固形分の75.95%、Mn800、Mw2500g/mol、Tg83°C）；熱酸生成剤としてブロックされたドデシルベンゼンスルホン酸9.520g、（King Industries, Norwalk, Connecticut, から販売されるNacure5225、イソプロパノール中25%固形分、固形分の2%）；架橋剤としてテトラブトキシグリコールウリル（26.180g、固形分の22%）；表面活性平滑剤FC430（3M, Minneapolis, Minnesota



から販売される、PGMEA中1%溶液、5.950g、固形分の0.05%）；ジメチルアジペート（5.950g、これを含まない固形分の5%）；およびPGMEAの322.512g。これにより固形分17%のサンプル700gを得た。組成物を物質が溶解されるのに十分な時間ロール（roll）し、使用前に0.2ミクロンのポリ（テトラフルオロエチレン）（PTFE）フィルターを通してろ過した。

#### 【0067】実施例2

P/CVD誘電体層を含む4つのウェハー（サンプル1-4）を、TEL Mark 8を使用して、実施例1のバリア組成物で種々の厚さでスピコートした。組成物を195℃で60秒、バイクした。市販の反射防止コーティング（AR7、Shipley Company, Marlborough, Massachusetts 製）を、硬化されたバリア組成物の表面上にスピコーティングし、600オングストロームの厚さとし、ついで

175℃で60秒バイクしてフィルムを硬化した。同じP/CVD誘電体層を有する4つのウェハー（比較サンプルC1-C4）を、同じくAR7反射防止コーティングで種々の厚さでスピコーティングし、同じ条件でバイクした。これらの比較サンプルはバリア組成物を含んでいない。すべてのウェハーを市販のフォトレジスト（UV210、Shipley Company 製）でスピコーティングした。フォトレジストは5000オングストロームの厚さにコーティングされ、130℃で60秒バイクされた。ついでウェハーはASML 5500/200を使用し、25mJ/cm<sup>2</sup>から33mJ/cm<sup>2</sup>で露光し、アスペクト比が1:2の200nmのトレンチを調製した。露光に引き続いて、ウェハーを130℃で90秒バイクし、ついで現像した。結果を表1に示す。

#### 【0068】

##### 【表1】

表 1

サンプル	バリア組成物 厚さ (Å)	反射防止コーティング 厚さ (Å)	露光結果
1	1300	600	イメージされた
2	1000	600	イメージされた
3	700	600	イメージされた
4	400	600	イメージされた
C-1	0	1300	イメージされなかった
C-2	0	1000	イメージされなかった
C-3	0	1600	ほとんど識別できない イメージであった
C-4	0	1900	イメージされたが、最小 照射量ではなかった

【0069】上記のデータは、本発明のバリア組成物が誘電体層によるフォトレジスト層のポイズニングまたはコンタミネーションを減少または防止するのに有効であることを明確に示している。さらに、本発明の組成物を使用する際、反射防止コーティング層の厚さを減少させることができる。

#### 【0070】実施例3

P/CVD誘電体層を有する4つのウェハー（サンプル5-8）を、実施例1のバリア組成物で種々の厚さでスピコートした。組成物を205℃で60秒、バイクした。市販の反射防止コーティング（AR3、Shipley Company 製）を、硬化されたバリア組成物の表面上にスピコーティングし、600オングストロームの厚さとし、ついで205℃で60秒バイクしてフィルムを硬化した。同じP/CVD誘電体層を有する1つのウェハー（比較サンプルC5）を、同じくAR3反射防止コーティングで600オングストロームの厚さ

でスピコーティングし、同じ条件でバイクした。これらの比較サンプルはバリア組成物を含んでいない。それぞれのウェハーを市販のフォトレジスト（UV200、Shipley Company 製）でスピコーティングした。フォトレジストは5000オングストロームの厚さにコーティングされ、プロキシミティ ホットプレート（proximity hotplate）を使用して、140℃で60秒バイクされた。ついでウェハーはASML 5500/300を使用して露光し、0.22ミクロンのコンタクトホールを調製した。露光に引き続いて、ウェハーを140℃で90秒、プロキシミティ ホットプレートを使用してバイクし、ついで現像した。現像後、ウェハーを走査電子顕微鏡（SEM）で評価した。図1-5は形成されたコンタクトホールの断面図を示す。露光条件および結果を表2に示す。

#### 【0071】

##### 【表2】

表 2

サンプル	バリア組成物 厚さ (Å)	$E_0$ (mJ/cm <sup>2</sup> )	$E_s$ (mJ/cm <sup>2</sup> )	図
5	600	5.0	33.0	2
6	1000	5.0	29.5	3
7	1500	5.0	34.5	4
8	2000	5.0	33.0	5
C-5	0	5.9	-	1

【0072】本発明のバリア組成物の使用は、バリア組成物を使用しないで形成されたものと比較して、良好なサイドウォール輪郭 (sidewall definition) とボーイングの少ないコンタクトホールを提供する。たとえば、図1は比較サンプルC-5によるコンタクトホールの断面写真であり、これは顕著なボーイングを示す。対照的に、図2-5は本発明のバリア組成物を使用して形成されたコンタクトホールの断面写真である。これらの写真では、コンタクトホールは良好なサイドウォール輪郭を有し、有意に少ないボーイングを有することを明確に示している。

【図面の簡単な説明】

【図1】図1はバリア層を使用しないで形成された誘電体層中のコンタクトホールの、SEMの断面写真であ

る。

【図2】図2は600オングストロームのバリア層を使用して形成された誘電体層中のコンタクトホールの、SEMの断面写真である。

【図3】図3は1000オングストロームのバリア層を使用して形成された誘電体層中のコンタクトホールの、SEMの断面写真である。

【図4】図4は1500オングストロームのバリア層を使用して形成された誘電体層中のコンタクトホールの、SEMの断面写真である。

【図5】図5は2000オングストロームのバリア層を使用して形成された誘電体層中のコンタクトホールの、SEMの断面写真である。

【図1】

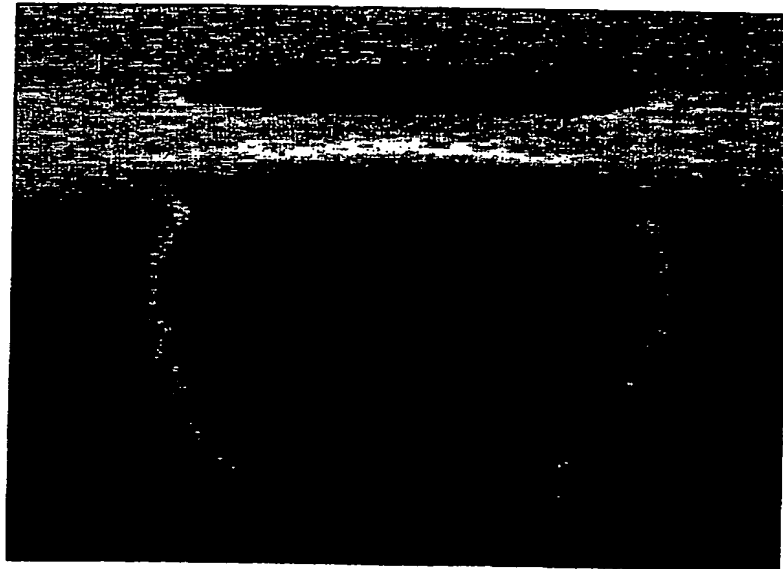


図 1

【図2】

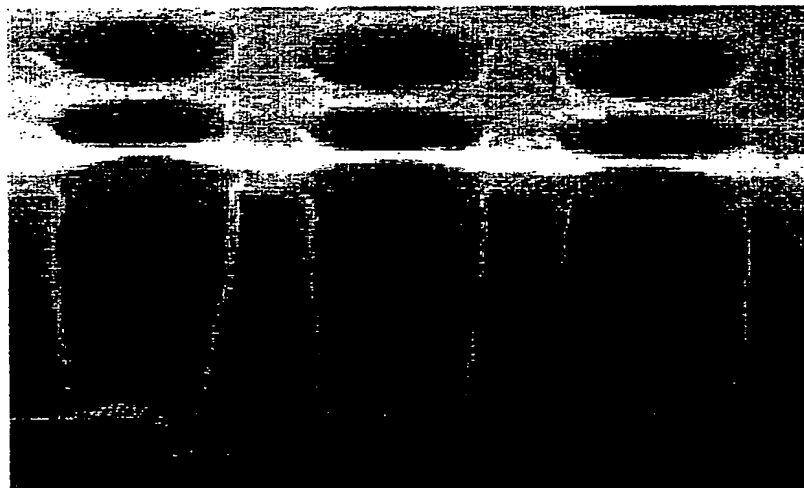


図 2

【図3】



図 3

【図4】

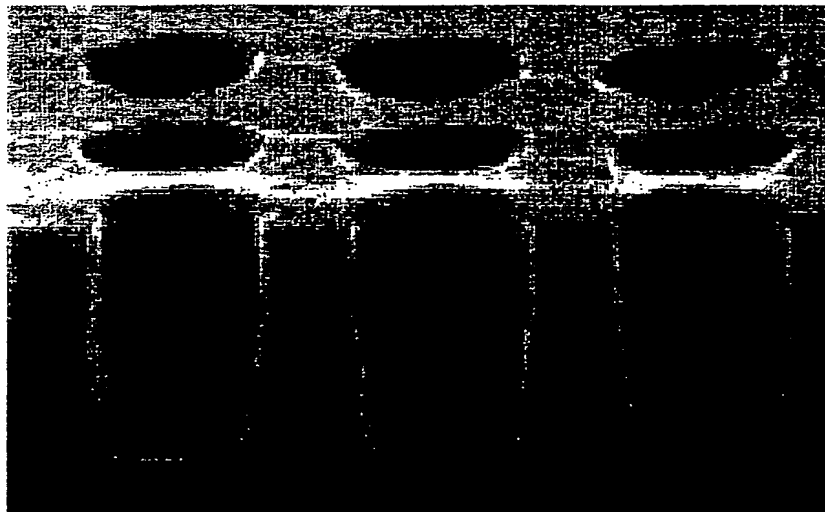


図 4

【図5】

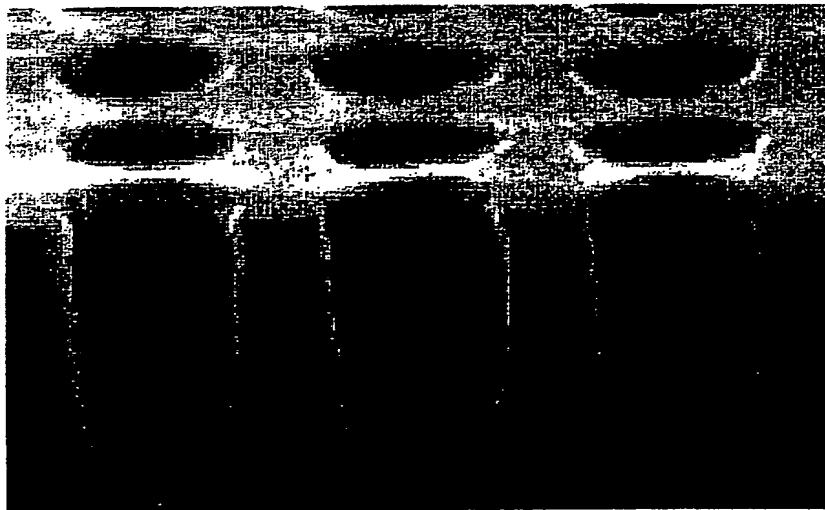


図 5

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フロントページの続き

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102

F ターム(参考) 2H025 AB16 AB17 AC04 AC05 AC06  
AC08 AD01 AD03 DA34 DA40  
4J026 AA45 AA46 AA47 AA48 AB01  
BA07 BA27 BA28 BA30 BA43  
DB06 DB09 DB11 DB24 DB36  
FA05 FA09 GA06 GA07 GA08  
4M104 DD06 DD62  
5F033 QQ02 QQ37

【外国語明細書】

1. Title of Invention

**BARRIER LAYER**

## 2. Claims

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What is claimed is:

1. A barrier composition comprising one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent comprises one or more acidic moieties.
2. The composition of claim 1 wherein the cross-linkable polymer comprises as polymerized units one or more aromatic hydroxyl compounds.
3. The composition of claim 1 wherein the cross-linkable polymer comprises one or more aromatic-aldehyde condensates.
4. The composition of claim 1 wherein the acidic moieties are at least partially free of blocking groups.
5. The composition of claim 1 wherein the cross-linkable polymer comprises one or more aromatic-aldehyde condensates and one or more (meth)acrylate polymers.
6. A method of providing a barrier layer on a dielectric substrate comprising the step of disposing on the surface of a dielectric substrate a composition comprising one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent comprises one or more acidic moieties.
7. The method of claim 6 wherein the cross-linkable polymer comprises as polymerized units one or more aromatic hydroxyl compounds.
8. The method of claim 6 wherein the cross-linkable polymer comprises one or more aromatic-aldehyde condensates.
9. The method of claim 6 wherein the acidic moieties are at least partially free of blocking groups.
10. The method of claim 6 wherein the cross-linkable polymer comprises one or more aromatic-aldehyde condensates and one or more (meth)acrylate polymers.
11. The method of claim 6 wherein the dielectric substrate is applied by physical vapor deposition or chemical vapor deposition.

12. The method of claim 6 wherein the dielectric substrate is inorganic.
13. The method of claim 6 wherein the dielectric substrate comprises silicon.
14. A device having a dielectric layer and a barrier layer disposed thereon, wherein the barrier layer comprises one or more cross-linked polymers comprising as polymerized units one or more cross-linkable polymers and one or more cross-linking agents, wherein at least one of the cross-linkable polymers and the cross-linking agent comprises one or more acidic moieties.
  15. The device of claim 14 further comprising a photoresist layer.
  16. The device of claim 14 further comprising an antireflective coating disposed between the barrier layer and the photoresist layer.
  17. The device of claim 14 wherein the barrier layer has a thickness of from about 200 Å to about 1.5 μm.
  18. The device of claim 14 wherein the dielectric layer is applied by physical vapor deposition or chemical vapor deposition.
  19. The device of claim 14 wherein the dielectric layer is inorganic.
  20. The device of claim 14 wherein the dielectric layer comprises silicon.
  21. A method of reducing contamination of a photoresist layer comprising the step of disposing a barrier layer between a dielectric layer and the photoresist layer, the barrier layer comprising one or more cross-linked polymers comprising as polymerized units one or more cross-linkable polymers and one or more cross-linking agents, wherein at least one of the cross-linkable polymers and the cross-linking agent comprises one or more acidic moieties.
    22. The method of claim 21 wherein the cross-linkable polymer comprises as polymerized units one or more aromatic hydroxyl compounds.
    23. The method of claim 21 wherein the cross-linkable polymer comprises one or more aromatic-aldehyde condensates.
    24. The method of claim 21 wherein the acidic moieties are at least partially free of blocking groups.



25. The method of claim 21 wherein the cross-linkable polymer comprises one or more aromatic-aldehyde condensates and one or more (meth)acrylate polymers.

26. The method of claim 21 wherein the dielectric layer is inorganic.

27. The method of claim 21 wherein the dielectric layer comprises silicon.

28. The method of claim 21 wherein the barrier layer has a thickness of from about 200 Å to about 1.5 μm.

29. A method for manufacturing an electronic device comprising the steps of: a) providing a dielectric layer on a substrate; b) disposing on a surface of the dielectric layer a barrier composition comprising one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent comprises one or more acidic moieties; and c) heating the substrate at a temperature sufficient to at least partially cure the barrier composition to form a barrier layer.

30. A method for manufacturing an electronic device comprising the steps of: a) providing a dielectric layer on a substrate; b) disposing on a surface of the dielectric layer a barrier composition comprising one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent comprises one or more acidic moieties; c) heating the substrate at a temperature sufficient to at least partially cure the barrier composition to form a barrier layer; d) disposing on the surface of the barrier layer an antireflective coating; and e) disposing on the surface of the antireflective coating a photoresist layer.

### 3. Detailed Description of Invention

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#### Background of the Invention

The present invention relates generally to the field of manufacture of electronic devices. In particular, the present invention relates to photoresists and antireflective coatings used in the manufacture of electronic devices.

In the manufacture of electronic devices, such as printed wiring boards or semiconductors, a number of layers of material, such as photoresists or antireflective coatings, are applied to a substrate. Photoresists are photosensitive films used for transfer of an image to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed through a photomask (reticle) to a source of activating radiation. The photomask has areas that are opaque to activating radiation and other areas that are transparent to activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask to the photoresist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate.

A photoresist can be either positive-acting or negative-acting. For most negative-acting photoresists, those coating layer portions that are exposed to activating radiation polymerize or cross-link in a reaction between a photoactive compound and polymerizable reagents of the photoresist composition. Consequently, the exposed coating portions are rendered less soluble in a developer solution than unexposed portions. For a positive-acting photoresist, exposed portions are rendered more soluble in a developer solution while areas not exposed remain comparatively less developer soluble. Photoresist compositions are known to the art and described by Deforest, Photoresist Materials and Processes, McGraw Hill Book Company, New York, ch. 2, 1975 and by Moreau, Semiconductor Lithography, Principles, Practices and Materials, Plenum Press, New York, ch. 2 and 4, both incorporated herein by reference to the extent they teach photoresist compositions and methods of making and using them.

## 2

A major use of photoresists is in the manufacture of semiconductors where an object is to create features, such as vias, trenches or combinations thereof, in a dielectric layer. Proper photoresist processing is a key to attaining this object. While there is a strong interdependency among the various photoresist processing steps, exposure is believed to be one of the more important steps in attaining high resolution photoresist images.

In such processes, reflection of actinic radiation during exposure of the photoresist and "poisoning" of the photoresist by the dielectric layer are detrimental to fine feature formation. Reflection of actinic radiation, such as from the layer underlying the photoresist, often poses limits on resolution of the image patterned in the photoresist layer. Reflection of radiation from the substrate/photoresist interface can produce variations in the radiation intensity in the photoresist during exposure, resulting in non-uniform photoresist linewidth upon development. Radiation also can scatter from the substrate/photoresist interface into regions of the photoresist where exposure is not intended, again resulting in linewidth variations. The amount of scattering and reflection will typically vary from region to region, resulting in further linewidth non-uniformity.

Reflection of activating radiation also contributes to what is known in the art as the "standing wave effect." To eliminate the effects of chromatic aberration in exposure equipment lenses, monochromatic or quasi-monochromatic radiation is commonly used in photoresist projection techniques. Due to radiation reflection at the photoresist/substrate interface, however, constructive and destructive interference is particularly significant when monochromatic or quasi-monochromatic radiation is used for photoresist exposure. In such cases the reflected light interferes with the incident light to form standing waves within the photoresist. In the case of highly reflective substrate regions, the problem is exacerbated since large amplitude standing waves create thin layers of underexposed photoresist at the wave minima. The underexposed layers can prevent complete photoresist development causing edge acuity problems in the photoresist profile. The time required to expose the photoresist is generally an increasing function of photoresist thickness because of the increased total amount of radiation required to expose an increased amount of photoresist. However, because of the standing wave effect, the time of exposure also includes a harmonic component which varies

between successive maximum and minimum values with the photoresist thickness. If the photoresist thickness is non-uniform, the problem becomes more severe, resulting in variable linewidths.

With recent trends towards high-density semiconductor devices, there is a movement in the industry to shorten the wavelength of exposure sources to deep ultraviolet (DUV) light (300 nm or less in wavelength), KrF excimer laser light (248 nm), ArF excimer laser light (193 nm), electron beams and soft x-rays. The use of shortened wavelengths of light for imaging a photoresist coating has generally resulted in increased reflection from the upper resist surface as well as the surface of the underlying substrate. Thus, the use of the shorter wavelengths has exacerbated the problems of reflection from a substrate surface.

An approach used to reduce the problem of reflected radiation has been the use of a radiation absorbing layer either interposed between the substrate surface and the photoresist coating layer, called a bottom antireflective coating or BARC, or a radiation layer disposed on the surface of the photoresist layer, called a top antireflective coating or TARC. See, for example, PCT Application WO 90/03598, EPO Application No. 0 639 941 A1 and U.S. Pat. Nos. 4,910,122, 4,370,405 and 4,362,809, all incorporated herein by reference to the extent they teach antireflective (antihalation) compositions and the use of the same. Such BARC and TARC layers have also been generally referred to in the literature as antireflective layers or antireflective compositions. Typically, such antireflective compositions include a radiation absorbing component (or chromophore) a polymeric binder and one or more cross-linking agents. For example, conventional antireflective compositions typically include an epoxy-phenol binder having no free hydroxyl groups or an acrylate binder substantially free of acid groups.

Variations in substrate topography also give rise to resolution-limiting reflection problems. Any image on a substrate can cause impinging radiation to scatter or reflect in various uncontrolled directions, affecting the uniformity of photoresist development. As substrate topography becomes more complex with efforts to design more complex circuits, the effects of reflected radiation become more critical. For example, metal

interconnects used on many microelectronic substrates are particularly problematic due to their topography and regions of high reflectivity.

One method of solving such problems resulting from variations in substrate topography is by placing a photoresist at the same height over a surface, as disclosed in U.S. Patent No. 4,557,797 (Fuller et al.). This patent uses a multi-layer structure having a relatively thick bottom layer of poly(methyl methacrylate) ("PMMA") to provide a planar surface, a thin middle layer of an antireflective coating and a thin top layer of a photoresist material. However, this system results in a thick polymer layer which must subsequently be removed. Such layers are typically removed by a variety of methods, such as chemical mechanical polishing ("CMP"), etching and wet chemical methods. Due to the added time and cost of such removal processes, it is desired that the polymer layers be as thin as possible to aid in their subsequent removal.

Another approach to solving the problems associated with variations in substrate topography is that disclosed in Adams et al., *Planarizing AR for DUV Lithography, Microlithography 1999: Advances in Resist Technology and Processing XVI*, Proceedings of SPIE, vol. 3678, part 2, pp 849-856, 1999, which discloses the use of a planarizing antireflective coating, which reduces the need for a separate planarizing layer disposed between the antireflective layer and the substrate.

The use of photoresist layers on dielectric layers often results in "poisoning" of the photoresist layer. This is particularly problematic when the dielectric layer is applied by physical or chemical vapor deposition ("P/CVD") techniques. While the theory of such poisoning is not fully understood, such dielectric layers may cause a significant photospeed shift, lifting, profile degradation or complete dissolution inhibition in previously patterned aperture regions, such as via regions during trench delineation in dual damascene processes. Such poisoning is particularly problematic when positive acting photoresists are used, such as in deep ultraviolet ("DUV") photoresists. While BARCs provide an effective chemical barrier for photoresist layers, such BARCs have not been completely effective in providing a barrier layer against such poisoning by dielectric layers.

There is thus a need to provide effective barriers to the poisoning effect of photoresists by dielectric layers and particularly barrier layers that also provide a planarized surface.

#### Summary of the Invention

It has been surprisingly found that the present invention substantially reduces or eliminates the contamination or poisoning effects of photoresist layers by dielectric layers. It has also been surprisingly found that the compositions of the present invention form substantially locally planarized surfaces. It has further been surprisingly found that the present invention substantially reduces or eliminates standing wave effects, bowing, top erosion, and footing.

In one aspect, the present invention provides a barrier composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties.

In a second aspect, the present invention provides a method of providing a barrier layer on a dielectric substrate including the step of disposing on the surface of a dielectric substrate a composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties.

In a third aspect, the present invention provides a device having a dielectric layer and a barrier layer disposed thereon, wherein the barrier layer includes one or more cross-linked polymers including as polymerized units one or more cross-linkable polymers and one or more cross-linking agents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties.

In a fourth aspect, the present invention provides a method of reducing contamination of a photoresist layer including the step of disposing a barrier layer between a dielectric layer and the photoresist layer, the barrier layer including one or

more cross-linked polymers including as polymerized units one or more cross-linkable polymers and one or more cross-linking agents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties.

In a fifth aspect, the present invention provides a method for manufacturing an electronic device including the steps of: a) providing a dielectric layer on a substrate; b) disposing on a surface of the dielectric layer a barrier composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties; and c) heating the substrate at a temperature sufficient to at least partially cure the barrier composition to form a barrier layer.

In a sixth aspect, the present invention provides a method for manufacturing an electronic device including the steps of: a) providing a dielectric layer on a substrate; b) disposing on a surface of the dielectric layer a barrier composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties; c) heating the substrate at a temperature sufficient to at least partially cure the barrier composition to form a barrier layer; d) disposing on the surface of the barrier layer an antireflective coating; and e) disposing on the surface of the antireflective coating a photoresist layer.

#### Brief Description of the Drawings

Fig. 1 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed without the use of a barrier layer.

Fig. 2 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 600 Å barrier layer.

Fig. 3 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 1000 Å barrier layer.

Fig. 4 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 1500 Å barrier layer.

Fig. 5 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 2000 Å barrier layer.

#### Detailed Description of the Invention

As used throughout this specification, the following abbreviations shall have the following meanings, unless the context clearly indicates otherwise: ° C = degrees Centigrade; g = gram; cm = centimeter; Å = angstroms; rpm = revolutions per minute; %wt = percent by weight; mol% = mole percent; mJ = milliJoules; cm<sup>2</sup> = square centimeters; L = liter and mL = milliliter.

The term "polymer" refers to dimers, trimers, tetramers, oligomers, homopolymers, copolymers and the like. "Monomer" refers to any ethylenically or acetylenically unsaturated compound capable of being polymerized. The term "(meth)acrylic" includes both acrylic and methacrylic and the term "(meth)acrylate" includes both acrylate and methacrylate. Likewise, the term "(meth)acrylamide" refers to both acrylamide and methacrylamide. "Alkyl" includes straight chain, branched and cyclic alkyl groups. "Cross-linker" and "cross-linking agent" are used interchangeably throughout this specification. "Apertures" refer to vias, trenches, and combinations thereof. "Features" refer to various geometries, including apertures.

All amounts are percent by weight and all ratios are by weight, unless otherwise noted. All numerical ranges are inclusive and combinable.

The present invention is directed to providing a substrate having a dielectric layer, particularly a PVD or CVD deposited dielectric layer, with a barrier layer. The present invention is further directed to reducing or eliminating the poisoning, or contamination, of a photoresist or antireflective coating layer by a dielectric layer. The present invention is particularly suited for use in any electronic device manufacturing process where a photoresist, antireflective coating or both are applied to a dielectric layer substrate.



The compositions of the present invention useful as barrier layer compositions include one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties. "Acidic moieties" refer to one or more acidic groups present on the cross-linkable polymers, cross-linking agents or both. The acidic moieties are at least partially free, preferably substantially free, and more preferably free of blocking groups. The term "free of blocking groups" refers to acidic moieties that have not been functionalized or reacted to form blocked acidic groups, such as ethers or esters. "Substantially free of blocking groups" refers to acidic moieties wherein  $\geq 50\%$  of the acidic groups have not been functionalized or reacted to form blocked acidic groups. It is preferred that  $\geq 30\%$  of the acidic groups have not been functionalized to form blocked acidic groups and more preferably  $\geq 20\%$ . Such acidic moieties include, but are not limited to, carboxylic acids, sulfonic acids, phosphonic acids, hydroxyl compounds such as aromatic hydroxyl compounds, anhydrides and the like. It is preferred that the acidic moieties include aromatic hydroxyl compounds.

It is preferred that the cross-linkable polymers include as polymerized units one or more monomers having acidic moieties, and more preferably one or more aromatic hydroxyl containing monomers. In such cross-linkable polymers, the monomers having acidic moieties are typically present in an amount of from about 1 to about 99 mol%, preferably at least about 3 mol%, more preferably at least about 5 mol%, and even more preferably at least about 10 mol%. Particularly suitable cross-linkable polymers include those having as polymerized units at least about 20, 30, 40, 50, 60, 70, 80 and 90 mol% of monomers having acidic moieties.

The cross-linkable polymers and cross-linking agents having acidic moieties useful in the present invention may also contain other functionality. Suitable other functionality includes, but is not limited to, ester groups, halogen, cyano, (C<sub>1</sub>-C<sub>6</sub>)alkoxy, and the like. Such polymers and cross-linking agents may also contain more than one acidic moiety, such as, for example, more than one aromatic hydroxyl group or a combination of an aromatic hydroxyl group and a carboxylic acid.

Typically, the cross-linkable polymers have a weight average molecular weight of about 8000 or less, preferably about 5000 or less, and more preferably about 3000 or less. It is also preferred that the cross-linkable polymers have a weight average molecular weight of at least about 300, preferably at least about 400, and more preferably at least about 500. Thus, a particularly useful weight average molecular weight range is from about 300 to about 8000, and more particularly from about 300 to about 5000.

The cross-linkable polymers of the present invention have low molecular weights and broad molecular weight distributions. The molecular weight distributions of the present invention are characterized by the polydispersity of the polymers, i.e. the ratio of the weight average molecular weight to number average molecular weight (" $M_w/M_n$ "). the polymers of the present invention typically have a value of  $M_w/M_n$ , i.e. polydispersity, of at least 1.5, preferably at least 1.8, more preferably at least 2.0, still more preferably at least 2.5, even more preferably at least 3.0 and most preferably at least 3.5. Typical polydispersities of such cross-linkable polymers are in the range of from 1.5 to 4, preferably 1.8 to 4, and more preferably 2 to 4.

Suitable cross-linkable polymers include, but are not limited to, aromatic-aldehyde condensates and any polymers including as polymerized units one or more hydroxyl group containing monomers such as poly(vinylphenol). The aromatic-aldehyde condensates useful in the present invention include, but are not limited to, phenolic novolak resins. Such novolak resins are typically prepared by condensation of a phenol with an aldehyde and are well known in the art and described in numerous publications including the Kirk Othmer Encyclopedia of Chemical Technology, Volume 15, pages 176 to 208, 1968, incorporated herein by reference to the extent it teaches such resins. Although phenol itself is the commonly used phenol for the formation of such phenolic resins, other hydroxy-substituted aromatic compounds are equally suitable, such as but not limited to resorcinol, alkyl substituted phenols such as naphthols, cresols, xlenols, and p-tert-butylphenol, and bisphenols such as p-phenylphenol and 4,4'-isopropylidenediphenol. Preferred phenols include the cresols, and more preferably m-cresol, mixtures of m- and p-cresol, 2,5-xlenol and mixtures thereof. Mixtures of hydroxy-substituted aromatic compounds may be advantageously used in the present invention.

The aldehyde used is typically formaldehyde, but other aldehydes such as but not limited to acetaldehyde, furfuraldehyde and aromatic aldehydes may be used. Preferred aromatic aldehydes are those where a hydroxyl group is in a position ortho to the carbonyl group. Most preferred aromatic aldehydes are salicylaldehyde, benzaldehyde and mixtures thereof. Other aromatic aldehydes suitable for purposes of the invention include 2-chlorobenzaldehyde, 3-hydroxybenzaldehyde, 4-hydroxybenzaldehyde, 2-methoxybenzaldehyde, 3-nitrobenzaldehyde, and the like. Mixtures of aldehydes may be advantageously used in the present invention. When an aromatic aldehyde is mixed with formaldehyde or a formaldehyde precursor such as paraformaldehyde, the aromatic aldehyde preferably is in molar excess of formaldehyde, and more preferably at least 90% by weight of the aldehyde mixture.

Typically, the phenol novolak resins are formed by condensing the phenol, i.e. hydroxy-substituted aromatic compound, with the aldehyde in the presence of acid. The molar concentration of the aldehyde may be slightly less than that of the phenol, but may also be equivalent to or slightly in excess of the phenol without formation of a crosslinked resin. In this respect, the ratio of the phenol to the aldehyde may vary between about 1.1 to 1.0 and 1.0 to 1.1 See, for example, U.S. Patent No. 5,939,511 (Zampini et al.).

In general, the polydispersity of such aromatic-aldehyde condensates useful as cross-linkable polymers in the present invention is at least about 2.5, preferably at least about 3.0 and more preferably at least about 3.5.

Any hydroxyl group containing ethylenically or acetylenically unsaturated compound is useful as the hydroxyl group containing monomer in the present invention. Such hydroxy group containing monomers may be aliphatic or aromatic, and preferably aromatic. Suitable hydroxy group containing monomers include, but are not limited to, phenol, cresol, resorcinol, pyrogallol, methylol phenol, methylol cresol, methylol resorcinol, methylol pyrogallol, hydroxyethylphenol, hydroxypropylphenol, hydroxyethylcresol, vinyl phenol, vinyl cresol, vinyl methoxy phenol, hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, hydroxycyclohexyl (meth)acrylate, hydroxyphenyl (meth)acrylate, di-ethyleneglycol

(meth)acrylate, bis(hydroxyethyl) itaconate, bis(hydroxyethyl) citraconate, bis(hydroxyethyl) fumarate, hydroxyethyl itaconate, allyl phenol, allyl methoxy phenol, allyl alcohol, vinyl alcohol, and the like.

It is preferred that the cross-linkable polymers of the present invention include as polymerized units one or more aromatic compounds, such as at least about 3 mol%, preferably at least about 5 mol%, and more preferably at least about 10 mol%. Preferred aromatic compounds include, but are not limited to, phenolic compounds, cresolic compounds, resorcinolic compounds, xylenolic compounds and the like. Particularly useful cross-linkable polymers include those containing at least about 20 mol% aromatic compounds as polymerized units. It is further preferred that the cross-linkable polymers include one or more aromatic-aldehyde condensates.

Particularly useful cross-linkable polymers include one or more aromatic-aldehyde condensates and one or more other polymers, such as (meth)acrylate polymers, wherein the value of  $M_w/M_n$  for the aromatic-aldehyde condensates is at least 2.5, and preferably at least 3.0. An advantage of including a non-aromatic polymer, such as a (meth)acrylate polymer, with the aromatic-aldehyde condensates is that the etch rate of the barrier composition may be increased. It is still further preferred that the cross-linkable polymers of the present invention are substantially free of silphenylene moieties, and more preferably free of silphenylene moieties.

Other monomers useful in preparing the cross-linkable polymers of the present invention include, but are not limited to, (meth)acrylic acid, (meth)acrylamides, alkyl (meth)acrylates, alkenyl (meth)acrylates, aromatic (meth)acrylates, vinyl aromatic monomers, nitrogen-containing compounds and their thio-analogs, substituted ethylene monomers, and the like. Particularly suitable cross-linkable polymers useful in the present invention include mixtures of aromatic-aldehyde condensates, particularly novolak resins, with one or more of poly((meth)acrylic acid), poly((meth)acrylamide), poly(alkyl (meth)acrylate), poly(alkenyl (meth)acrylate), poly(aromatic (meth)acrylate), and poly(vinyl aromatic).

Typically, the alkyl (meth)acrylates useful in the present invention are (C<sub>1</sub>-C<sub>24</sub>) alkyl (meth)acrylates. Suitable alkyl (meth)acrylates include, but are not limited to, "low

cut" alkyl (meth)acrylates, "mid cut" alkyl (meth)acrylates and "high cut" alkyl (meth)acrylates.

"Low cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 1 to 6 carbon atoms. Suitable low cut alkyl (meth)acrylates include, but are not limited to: methyl methacrylate ("MMA"), methyl acrylate, ethyl acrylate, propyl methacrylate, butyl methacrylate ("BMA"), butyl acrylate ("BA"), isobutyl methacrylate ("IBMA"), hexyl methacrylate, cyclohexyl methacrylate, cyclohexyl acrylate and mixtures thereof.

"Mid cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 7 to 15 carbon atoms. Suitable mid cut alkyl (meth)acrylates include, but are not limited to: 2-ethylhexyl acrylate ("EHA"), 2-ethylhexyl methacrylate, octyl methacrylate, decyl methacrylate, isodecyl methacrylate ("IDMA", based on branched (C<sub>10</sub>)alkyl isomer mixture), undecyl methacrylate, dodecyl methacrylate (also known as lauryl methacrylate), tridecyl methacrylate, tetradecyl methacrylate (also known as myristyl methacrylate), pentadecyl methacrylate and mixtures thereof. Particularly useful mixtures include dodecyl-pentadecyl methacrylate ("DPMA"), a mixture of linear and branched isomers of dodecyl, tridecyl, tetradecyl and pentadecyl methacrylates; and lauryl-myristyl methacrylate ("LMA").

"High cut" alkyl (meth)acrylates are typically those where the alkyl group contains from 16 to 24 carbon atoms. Suitable high cut alkyl (meth)acrylates include, but are not limited to: hexadecyl methacrylate, heptadecyl methacrylate, octadecyl methacrylate, nonadecyl methacrylate, cosyl methacrylate, eicosyl methacrylate and mixtures thereof. Particularly useful mixtures of high cut alkyl (meth)acrylates include, but are not limited to: octyl-eicosyl methacrylate ("CEMA"), which is a mixture of hexadecyl, octadecyl, cosyl and eicosyl methacrylate; and cetyl-stearyl methacrylate ("SMA"), which is a mixture of hexadecyl and octadecyl methacrylate.

The mid-cut and high-cut alkyl (meth)acrylate monomers described above are generally prepared by standard esterification procedures using technical grades of long chain aliphatic alcohols, and these commercially available alcohols are mixtures of alcohols of varying chain lengths containing between 10 and 15 or 16 and 20 carbon

atoms in the alkyl group. Examples of these alcohols are the various Ziegler catalyzed ALFOL alcohols from Vista Chemical company, i.e., ALFOL 1618 and ALFOL 1620, Ziegler catalyzed various NEODOL alcohols from Shell Chemical Company, i.e. NEODOL 25L, and naturally derived alcohols such as Proctor & Gamble's TA-1618 and CO-1270. Consequently, for the purposes of this invention, alkyl (meth)acrylate is intended to include not only the individual alkyl (meth)acrylate product named, but also to include mixtures of the alkyl (meth)acrylates with a predominant amount of the particular alkyl (meth)acrylate named.

The alkyl (meth)acrylate monomers useful in the present invention may be a single monomer or a mixture having different numbers of carbon atoms in the alkyl portion. Also, the (meth)acrylamide and alkyl (meth)acrylate monomers useful in the present invention may optionally be substituted. Suitable optionally substituted (meth)acrylamide and alkyl (meth)acrylate monomers include, but are not limited to: hydroxy (C<sub>2</sub>-C<sub>6</sub>)alkyl (meth)acrylates, dialkylamino(C<sub>2</sub>-C<sub>6</sub>)-alkyl (meth)acrylates, dialkylamino(C<sub>2</sub>-C<sub>6</sub>)alkyl (meth)acrylamides.

Particularly useful substituted alkyl (meth)acrylate monomers are those with one or more hydroxyl groups in the alkyl radical, especially those where the hydroxyl group is found at the  $\beta$ -position (2-position) in the alkyl radical. Hydroxyalkyl (meth)acrylate monomers in which the substituted alkyl group is a (C<sub>2</sub>-C<sub>6</sub>)alkyl, branched or unbranched, are preferred. Suitable hydroxyalkyl (meth)acrylate monomers include, but are not limited to: 2-hydroxyethyl methacrylate ("HEMA"), 2-hydroxyethyl acrylate ("HEA"), 2-hydroxypropyl methacrylate, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxy-propyl acrylate, 1-methyl-2-hydroxyethyl acrylate, 2-hydroxybutyl methacrylate, 2-hydroxybutyl acrylate and mixtures thereof. The preferred hydroxyalkyl (meth)acrylate monomers are HEMA, 1-methyl-2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate and mixtures thereof. A mixture of the latter two monomers is commonly referred to as "hydroxypropyl methacrylate" or "HPMA."

Other substituted (meth)acrylate and (meth)acrylamide monomers useful in the present invention are those with a dialkylamino group or dialkylaminoalkyl group in the alkyl radical. Examples of such substituted (meth)acrylates and (meth)acrylamides

include, but are not limited to: dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, *N,N*-dimethylaminoethyl methacrylamide, *N,N*-dimethyl-aminopropyl methacrylamide, *N,N*-dimethylaminobutyl methacrylamide, *N,N*-diethylaminoethyl methacrylamide, *N,N*-diethylaminopropyl methacrylamide, *N,N*-diethylaminobutyl methacrylamide, *N*-(1,1-dimethyl-3-oxobutyl) acrylamide, *N*-(1,3-diphenyl-1-ethyl-3-oxobutyl) acrylamide, *N*-(1-methyl-1-phenyl-3-oxobutyl) methacrylamide, and 2-hydroxyethyl acrylamide, *N*-methacrylamide of aminoethyl ethylene urea, *N*-methacryloxy ethyl morpholine, *N*-maleimide of dimethylaminopropylamine and mixtures thereof.

Other substituted (meth)acrylate monomers useful in the present invention are silicon-containing monomers such as  $\gamma$ -propyl tri( $C_1$ - $C_6$ )alkoxysilyl (meth)acrylate,  $\gamma$ -propyl tri( $C_1$ - $C_6$ )alkylsilyl (meth)acrylate,  $\gamma$ -propyl di( $C_1$ - $C_6$ )alkoxy( $C_1$ - $C_6$ )alkylsilyl (meth)acrylate,  $\gamma$ -propyl di( $C_1$ - $C_6$ )alkyl( $C_1$ - $C_6$ )alkoxysilyl (meth)acrylate, vinyl tri( $C_1$ - $C_6$ )alkoxysilyl (meth)acrylate, vinyl di( $C_1$ - $C_6$ )alkoxy( $C_1$ - $C_6$ )alkylsilyl (meth)acrylate, vinyl ( $C_1$ - $C_6$ )alkoxydi( $C_1$ - $C_6$ )alkylsilyl (meth)acrylate, vinyl tri( $C_1$ - $C_6$ )alkylsilyl (meth)acrylate, and mixtures thereof.

The vinylaromatic monomers useful as unsaturated monomers in the present invention include, but are not limited to: styrene ("STY"),  $\alpha$ -methylstyrene, vinyltoluene, *p*-methylstyrene, ethylvinylbenzene, vinylnaphthalene, vinylxylenes, and mixtures thereof. The vinylaromatic monomers also include their corresponding substituted counterparts, such as halogenated derivatives, i.e., containing one or more halogen groups, such as fluorine, chlorine or bromine; and nitro, cyano, ( $C_1$ - $C_{10}$ )alkoxy, halo( $C_1$ - $C_{10}$ )alkyl, carb( $C_1$ - $C_{10}$ )alkoxy, carboxy, amino, ( $C_1$ - $C_{10}$ )alkylamino derivatives and the like.

The nitrogen-containing compounds and their thio-analogs useful as unsaturated monomers in the present invention include, but are not limited to: vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine; lower alkyl ( $C_1$ - $C_8$ ) substituted *N*-vinyl pyridines such as 2-methyl-5-vinyl-pyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinyl-pyridine, and 2-methyl-3-ethyl-5-vinylpyridine; methyl-substituted quinolines and isoquinolines; *N*-vinylcaprolactam; *N*-vinylbutyrolactam; *N*-

vinylpyrrolidone; vinyl imidazole; N-vinyl carbazole; N-vinyl-succinimide; (meth)acrylonitrile; *o*-, *m*-, or *p*-aminostyrene; maleimide; N-vinyl-oxazolidone; N,N-dimethyl aminoethyl-vinyl-ether; ethyl-2-cyano acrylate; vinyl acetonitrile; N-vinylphthalimide; N-vinyl-pyrrolidones such as N-vinyl-thio-pyrrolidone, 3 methyl-1-vinyl-pyrrolidone, 4-methyl-1-vinyl-pyrrolidone, 5-methyl-1-vinyl-pyrrolidone, 3-ethyl-1-vinyl-pyrrolidone, 3-butyl-1-vinyl-pyrrolidone, 3,3-dimethyl-1-vinyl-pyrrolidone, 4,5-dimethyl-1-vinyl-pyrrolidone, 5,5-dimethyl-1-vinyl-pyrrolidone, 3,3,5-trimethyl-1-vinyl-pyrrolidone, 4-ethyl-1-vinyl-pyrrolidone, 5-methyl-5-ethyl-1-vinyl-pyrrolidone and 3,4,5-trimethyl-1-vinyl-pyrrolidone; vinyl pyrroles; vinyl anilines; and vinyl piperidines.

The substituted ethylene monomers useful as unsaturated monomers in the present invention include, but are not limited to: allylic monomers, vinyl acetate, vinyl formamide, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, vinylidene fluoride and vinylidene bromide.

Cross-linkable polymers are present in the compositions of the invention across a wide range of amounts. Typically, the cross-linkable polymers are present in amounts of from about 40 to about 85 % of solids, and preferably from about 60 to about 85 % of solids.

Cross-linkers useful in the present invention are any which undergo acid catalyzed cross-linking with the cross-linkable polymers. Typically, the cross-linkers of the present invention have a molecular weight of about 120 Daltons or greater. It is preferred that the cross-linkers undergo cross-linking reactions a temperature from about 75° C to about 250° C. Suitable cross-linkers include di-, tri-, tetra-, or higher multi-functional ethylenically unsaturated monomers. Examples of cross-linkers useful in the present invention include, but are not limited to: trivinylbenzene, divinyltoluene, divinylpyridine, divinylnaphthalene and divinylxylene; and such as ethyleneglycol diacrylate, trimethylolpropane triacrylate, diethyleneglycol divinyl ether, trivinylcyclohexane, allyl methacrylate ("ALMA"), ethyleneglycol dimethacrylate ("EGDMA"), diethyleneglycol dimethacrylate ("DEGDMA"), propyleneglycol dimethacrylate, propyleneglycol diacrylate, trimethylolpropane trimethacrylate ("TMPTMA"), divinyl benzene ("DVB"), glycidyl methacrylate, 2,2-dimethylpropane



1,3 diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, tripropylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, polyethylene glycol 200 diacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, polyethylene glycol 600 dimethacrylate, poly(butanediol) diacrylate, pentaerythritol triacrylate, trimethylolpropane triethoxy triacrylate, glyceryl propoxy triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxypentaacrylate, divinyl silane, trivinyl silane, dimethyl divinyl silane, divinyl methyl silane, methyl trivinyl silane, diphenyl divinyl silane, divinyl phenyl silane, trivinyl phenyl silane, divinyl methyl phenyl silane, tetravinyl silane, dimethyl vinyl disiloxane, poly(methyl vinyl siloxane), poly(vinyl hydro siloxane), poly(phenyl vinyl siloxane), tetra(C<sub>1</sub>-C<sub>8</sub>)alkoxyglycoluril such as tetramethoxyglycoluril and tetrabutoxyglycoluril, and mixtures thereof.

The cross-linkers of the present invention may be used in the compositions of the present invention in a wide range of concentrations. Typically, the cross-linkers are present in amounts of from about 1 to about 30 % of solids, preferably from about 10 to about 25 % of solids, and more preferably from about 15 to about 25 % of solids.

The acid catalysts useful in the present invention are any which are capable of catalyzing the cross-linking reaction of the barrier layer compositions of the present invention and include free acids and acid generators. Examples of free acids include, but are not limited to, sulfonic acids such as methane sulfonic acid, ethane sulfonic acid, propyl sulfonic acid, phenyl sulfonic acid, toluene sulfonic acid, dodecylbenzene sulfonic acid, and trifluoromethyl sulfonic acid.

The acid generators include thermal acid generators ("TAGs"), photoacid generators ("PAGs") and mixtures thereof. Any thermal acid generator and any photoacid generator are useful in the present invention. A thermal acid generator is any compound that liberates acid upon thermal treatment. Suitable thermal acid generators include, but are not limited to, 2,4,4,6-tetrabromocyclohexadienone, benzoin tosylate, 2-

nitrobenzyl tosylate, other alkyl esters of organic sulfonic acids and amine salts of sulfonic acids, such as amine salts of dodecyl benzene sulfonic acid. Compounds that generate a sulfonic acid upon activation, i.e. exposure to heat, are generally suitable. Photoacid generators are compounds that liberate acid upon photolysis. Suitable photoacid generators include, but are not limited to, onium salts and halogenated non-ionic photoacid generators such as 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane and fluoroalkylsulfonic acids, such as perfluorooctylsulfonic acid.

The acid catalysts are typically present in the compositions of the present invention in an amount sufficient to catalyze the desired cross-linking reactions, such as from about 0.1 to about 8 % of solids, and preferably from about 0.5 to about 5 % of solids. It is preferred that a combination of acid catalysts is used in the present invention. Suitable combinations include a free acid with a photoacid generator and a free acid with a thermal acid generator. Such acid catalysts are generally known or commercially available and may be used without further purification.

The compositions of the present invention contain one or more solvents. Any solvent that is compatible with the formulation is suitable. Solvents having low viscosity are preferred. Suitable solvents include, but are not limited to, propylene glycol methyl ether acetate, 2-heptanone, ethyl lactate or one or more of the glycol ethers such as 2-methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; solvents that have both ether and hydroxy moieties such as methoxy butanol, ethoxy butanol, methoxy propanol and ethoxy propanol; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters, propylene carbonate and gamma-butyrolactone. Particularly suitable solvents useful in the present invention are relatively high boiling, i.e. such solvents have boiling points at least about 170° C, and preferably at least about 190° C. Mixtures of solvents may be advantageously used in the present invention. Thus, the solvents of the present invention may be admixed with one or more other solvents. Such other solvents may be high boiling or low boiling. When two or more solvents are used, it is preferred that at least one solvent has a boiling point in the range of from about 75° to about 200° C. It is further preferred that when two or more solvents are used, that at least one solvent has a

boiling point of less than about 200° C and at least one other solvent has a boiling point greater than about 200° C.

The compositions of the present invention may optionally include one or more other components, such as, but not limited to, plasticizers, surfactants, leveling agents, dyes, pigments, chromophores, and the like.

Plasticizers may be added to the compositions of the present invention to improve certain characteristics of the compositions. Suitable plasticizers include, but are not limited to, dibasic esters such as dimethyl adipate and dimethyl succinate. Mixtures of plasticizers may be used in the present invention. Typically, the plasticizers are used in an amount of from about 0.5 to about 10 % of solids, and preferably from about 1 to about 5 % of solids. It is preferred that one or more plasticizers are used in the compositions of the present invention. It will be appreciated by those skilled in the art that higher amounts of plasticizers, such as up to about 50 to about 100 % of solids, may be advantageously used in the present invention. It is preferred that the plasticizer is a liquid.

Optional surfactants include, but are not limited to, nonionic surfactants, cationic surfactants and mixtures thereof. Particularly suitable surfactants are fluorinated surfactants, such as those available from the 3M Company. Surfactants are typically used in an amount of from about 0.1 to about 1.0 %wt.

The leveling agents useful in the present invention are surface leveling agents such as those available under the tradename SILWET 7604 from Witco, or the surfactant FC 430 available from the 3M Company. The choice and amount of such leveling agent is within the ability of one skilled in the art. Typically, such leveling agents are used in an amount of from about 0.1 to about 2 % of total solids.

The compositions of the present invention may also function as antireflective coatings. For example, when the cross-linkable polymer and/or the cross-linking agent contains aromatic groups, such compositions may be used as an antireflective composition for 193 nm radiation. In the alternative, dyes or chromophores may be added to the compositions of the present invention, such as by copolymerization or admixture with, to provide antireflective compositions useful at other wavelengths of

radiation. For example, the cross-linkable polymer and/or cross-linking agent may contain sufficient chromophore groups to yield an optical density of from about 0.3 to about 0.8 at the exposure wavelength used for subsequently applied photoresist layers. In the alternative, a chromophore such as an anthracene compound, may be added directly to the present compositions.

The concentration of the dry components, i.e. one or more cross-linkable polymers, one or more acid catalysts and one or more cross-linking agents, in the solvent will depend on several factors such as the method of application. In general, the solids content of the compositions of the present invention include from about 0.5 to 25 weight percent of the total weight of the composition, preferably the solids content varies from about 2 to 20 weight percent of the total weight of the composition. The compositions of the present invention are prepared by combining the components in any order.

The compositions of the present invention are useful as a barrier layer on a substrate, particularly dielectric layer substrates, in the manufacture of electronic devices, such as semiconductors, conductors, integrated circuits, printed wiring boards, and the like. The compositions of the present invention are particularly useful in the manufacture of semiconductor devices such as wafers used in the manufacture of semiconductors. The compositions of the present invention may be applied to the substrate by any of a variety of means, such as by spin coating. When applied to a substrate, the compositions of the present invention provide a coating or layer disposed on the surface of the substrate. When the compositions are applied by spin coating, such as to a semiconductor wafer, the thickness of the resulting film can be controlled, such as from about  $<200 \text{ \AA}$  to about  $1.5 \text{ }\mu\text{m}$ , and preferably from about  $200 \text{ \AA}$  to about  $1.5 \text{ }\mu\text{m}$ . Typically, the barrier compositions of the present invention are applied in layers of from about 600 to about  $1600 \text{ \AA}$ , and preferably from about 600 to about  $1200 \text{ \AA}$ .

Thus, the present invention provides a method of providing a barrier layer on a dielectric substrate including the step of disposing on the surface of a dielectric substrate a composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties.

The barrier layers of the present invention may be advantageously used to reduce or eliminate the contamination of any photoresist or antireflective coating by any dielectric layer, preferably PVD or CVD deposited dielectric layers. Suitable dielectric layers include inorganic dielectric layers, organic dielectric layers and mixtures thereof, and preferably inorganic dielectric layers. Suitable inorganic dielectric layers include, but are not limited to, silicon containing dielectric materials such as silica, silsesquioxanes, partially condensed alkoxysilanes, organically modified silicates, and the like. Various organic dielectric materials may also be used in the present invention.

Typically, the compositions of the present invention are at least partially cured by heating at a temperature of from about 75° to about 250° C, preferably from about 90° to about 225° C. "At least partially cured" refers to at least about 10% cross-linking of the barrier composition. It is preferred that the barrier composition is substantially cross-linked and more preferably fully crosslinked. The compositions of the present invention may be cured by subjecting a substrate coated with the composition to a one-step or two-step bake. A one-step bake heats the compositions of the present invention at a temperature and for a period of time sufficiently to at least partially, and preferably substantially, cross-link the composition. In the alternative, a two-step bake may be used which heats the compositions of the present invention at a first temperature which is not sufficient to cure the compositions but allows the compositions to reflow to improve planarization, followed by heating at a second temperature and for a period of time sufficiently to at least partially, and preferably substantially, cross-link the composition.

In general, the compositions of the present invention are cured from about 15 to about 360 seconds, preferably from about 15 to about 120 seconds, more preferably from about 30 to about 120 seconds, and even more preferably about 60 seconds. It will be appreciated by those skilled in the art that the specific curing time will depend upon the specific cross-linking agent, amount of cross-linking agent, amount of acid catalyst, heating temperature, among others

Thus, the present invention also provides substrates or devices having a dielectric layer and a barrier layer disposed thereon, wherein the barrier layer includes one or more cross-linked polymers including as polymerized units one or more cross-linkable

polymers and one or more cross-linking agents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties. It is preferred that in such devices that a photoresist layer is disposed on the barrier layer. It is further preferred that an antireflective composition is disposed between the barrier layer and the photoresist layer.

In the manufacture of electronic devices, particularly semiconductor wafers, dielectric layers are often applied, such as by physical vapor deposition ("PVD") or chemical vapor deposition ("CVD"). These dielectric layers need to be patterned for subsequent etching and metallization steps. Such patterning is achieved through the use of photoresists, often in conjunction with antireflective coatings. The application of a layer of a barrier composition of the present invention prior to the application of the photoresist layer, and preferably prior to the application of an antireflective coating, greatly reduces or eliminates poisoning or contamination of the photoresist layer by the dielectric layer.

The poisoning or contamination of a photoresist layer is evidenced by reduced resolution of features. For example, Fig. 1 shows a scanning electron micrograph ("SEM") of a cross-sectional image of a contact hole in a dielectric layer formed without the use of a barrier layer. Significant bowing in the bottom of the contact hole can clearly be seen in this figure. When a barrier layer of the present invention is used, the poisoning or contamination of the photoresist layer, as evidenced by bowing, is greatly reduced or eliminated. Fig. 2 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 600 Å barrier layer of the present invention. A reduction in the amount of bowing in the bottom of the contact hole as compared to Fig. 1 is clearly visible. Thicker barrier layers of the present invention further reduce such poisoning or contamination. Figures 3 to 5 show a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 1000 Å, 1500 Å and 2000 Å thick barrier layer, respectively. As can be seen from Figures 2 through 5, the barrier layers of the present invention significantly reduce the poisoning or contamination of a photoresist layer, as evidenced by bowing.

Thus, the present invention provides a method for manufacturing an electronic device including the steps of: a) providing a dielectric layer on a substrate; b) disposing on a surface of the dielectric layer a barrier composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties; and c) heating the substrate at a temperature sufficient to at least partially cure the barrier composition to form a barrier layer. Typically, a photoresist layer is disposed on the surface of the barrier layer. It is preferred that an antireflective coating is disposed between the surface of the barrier layer and the photoresist layer. It is further preferred that the photoresist layer includes a positive acting photoresist.

Thus, the present invention provides a method for manufacturing an electronic device including the steps of: a) providing a dielectric layer on a substrate; b) disposing on a surface of the dielectric layer a barrier composition including one or more cross-linkable polymers, one or more acid catalysts, one or more cross-linking agents and one or more solvents, wherein at least one of the cross-linkable polymers and the cross-linking agent includes one or more acidic moieties; c) heating the substrate at a temperature sufficient to at least partially cure the barrier composition to form a barrier layer; d) disposing on the surface of the barrier layer an antireflective coating; and e) disposing on the surface of the antireflective coating a photoresist layer.

If a barrier layer of the present invention is used without an antireflective coating, it is preferred that the barrier layer has a thickness of at least about 1000 Å, more preferably at least about 1200 Å, and even more preferably at least about 1500 Å. When an antireflective coating is disposed between the barrier layer and the photoresist layer, it is preferred that the barrier layer has a thickness of at least about 400 Å, and more preferably of at least about 600 Å. Typical ranges of barrier thickness are from about 400 to about 2500 Å, preferably from about 600 to about 2000 Å, and more preferably from about 800 to about 1500 Å. In general, antireflective coatings have a thickness of from about 200 to about 2000 Å, and preferably from about 400 to about 1600 Å. Photoresist layers, in general, have a thickness of from about 200 to about 10,000 Å, preferably from about 500 to about 7500 Å.

An advantage of the compositions of the present invention is that they are spin bowl compatible with photoresist and spin-on dielectrics.

Although the invention has been described primarily with respect to semiconductor manufacture, it will be appreciated that the present invention may be used in a wide variety of applications.

The following examples are intended to illustrate further various aspects of the present invention, but are not intended to limit the scope of the invention in any aspect.

#### Example 1

A barrier layer composition was prepared by combining a meta-cresol-para-cresol-2,5-dimethoxyphenol novolak polymer (301.268 g of a 30 % solids solution in propylene glycol monomethyl ether acetate ("PGMEA"), 75.95% of solids, Mn 800, Mw 2500 g/mol, Tg 83° C), 9.520 g of a blocked dodecyl benzene sulfonic acid as a thermal acid generator, (Nacure 5225 available from King Industries, Norwalk, Connecticut, as a 25 % solids solution in iso-propanol, 2% of solids), tetrabutoxyglycoluril as cross-linking agent (26.180 g, 22 % of solids), FC430 (available from 3M, Minneapolis, Minnesota) as a surface active leveling agent (5.950 g of a 1% solution in PGMEA, 0.05% solids), dimethyl adipate (5.950 g, 5 % of solids without including it in solids calculation), and 322.512 g of PGMEA. This prepared a 700 g sample at 17 % solids. The composition was rolled for a period sufficient to solubilize the material and filtered through a 0.2 micron poly(tetrafluoroethylene) ("PTFE") filter prior to use.

#### Example 2

Four wafers containing a P/CVD dielectric layer (Samples 1-4) were spin coated with various thicknesses of the barrier composition of the Example 1 using a TEL Mark 8. The compositions were baked at 195° C for 60 seconds. A commercially available antireflective coating (AR7, available from Shipley Company, Marlborough, Massachusetts) was spin coated on the surface of the cured barrier composition to provide a thickness of 600 Å and then baked at 175° C for 60 seconds to cure the film.



Four wafers containing the same P/CVD dielectric layer (Comparative Samples C1-C4) were spin coated with the same AR7 antireflective coating at various thicknesses and baked under the same conditions. These comparative samples did not contain any barrier composition.

All the wafers were then spin coated with a commercially available photoresist (UV210, available from Shipley Company). The photoresist was coated to a thickness of 5000 Å and baked at 130° C for 60 seconds. The wafers were then exposed using an ASML 5500/200 tool at 25 mJ/cm<sup>2</sup> up to 33 mJ/cm<sup>2</sup> to prepare 200 nm trenches having an aspect ratio of 1:2. Following exposure, the wafers were baked at 130° C for 90 seconds and then developed. The results are reported in Table 1.

Table 1

Sample	Barrier Composition Thickness (Å)	Antireflective Coating Thickness (Å)	Exposure Results
1	1300	600	Imaged
2	1000	600	Imaged
3	700	600	Imaged
4	400	600	Imaged
C-1	0	1300	Did not image
C-2	0	1000	Did not image
C-3	0	1600	Barely discernible imaging
C-4	0	1900	Imaged, but not at lowest dose

The above data clearly show that the barrier compositions of the present invention are effective in reducing or preventing contamination or poisoning of photoresist layers by dielectric layers. Further, when the compositions of the present invention are used, the thickness of any antireflective coating layer may be reduced.

Example 3

Four wafers having a P/CVD dielectric layer (Samples 5-8) were spin coated with various thicknesses of the barrier composition of the Example 1. The compositions were baked at 205° C for 60 seconds. A commercially available antireflective coating (AR3, available from Shipley Company) was spin coated on the surface of the cured barrier composition to provide a thickness of 600 Å and then baked at 205° C for 60 seconds to cure the film. One wafer (Comparative Sample C-5) containing the same P/CVD dielectric layer was spin coated with the same AR3 antireflective coating at 600 Å thickness and baked under the same conditions. This comparative sample *did not* contain the barrier composition.

Each wafer was then spin coated with a commercially available photoresist (UV200, available from Shipley Company). The photoresist was coated to a thickness of 5000 Å and baked at 140° C for 60 seconds using a proximity hotplate. The wafers were then exposed using an ASML 5500/300 tool to prepare 0.22 μ contact holes. Following exposure, the wafers were baked at 140° C for 90 seconds using a proximity hotplate and then developed. After development, the wafers were examined using scanning electron microscopy ("SEM"). Figures 1-5 show the cross-sectional image of the contact holes formed. The exposure conditions and results are reported in Table 2.

Table 2

Sample	Barrier Composition Thickness (Å)	E <sub>0</sub> (mJ/cm <sup>2</sup> )	E <sub>t</sub> (mJ/cm <sup>2</sup> )	Figure
5	600	5.0	33.0	2
6	1000	5.0	29.5	3
7	1500	5.0	34.5	4
8	2000	5.0	33.0	5
C-5	0	5.9	-	1

The use of the barrier compositions of the present invention provide contact holes having better sidewall definition and less bowing than those formed without the use of the barrier composition. For example, Figure 1 shows the cross-sectional image of a

contact hole from Comparative Sample C-5, which shows significant bowing. In contrast, Figures 2-5 show cross-sectional images of contact holes formed using the barrier compositions of the present invention. In these figures, it can clearly be seen that the contact holes have better sidewall definition and significantly less bowing.

#### 4. Brief Description of the Drawings

Fig. 1 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed without the use of a barrier layer.

Fig. 2 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 600 Å barrier layer.

Fig. 3 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 1000 Å barrier layer.

Fig. 4 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 1500 Å barrier layer.

Fig. 5 shows a SEM of a cross-sectional image of a contact hole in a dielectric layer formed with the use of a 2000 Å barrier layer.

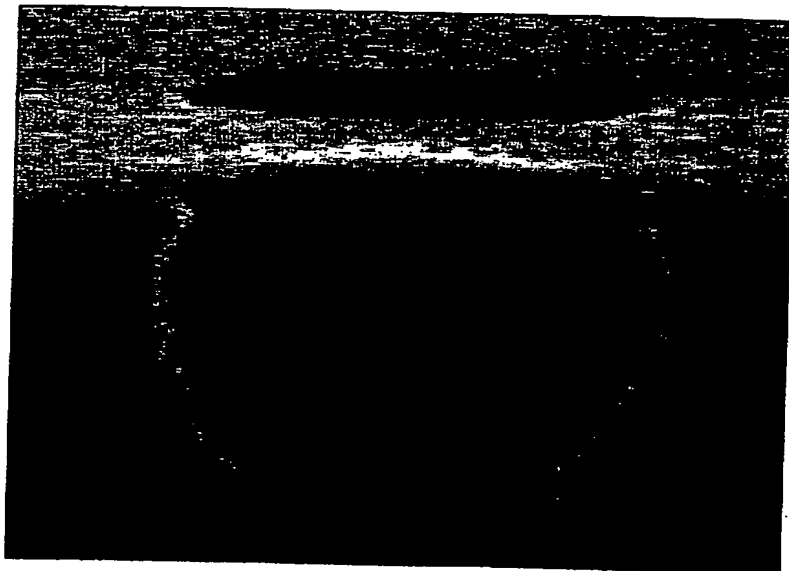


FIG. 1

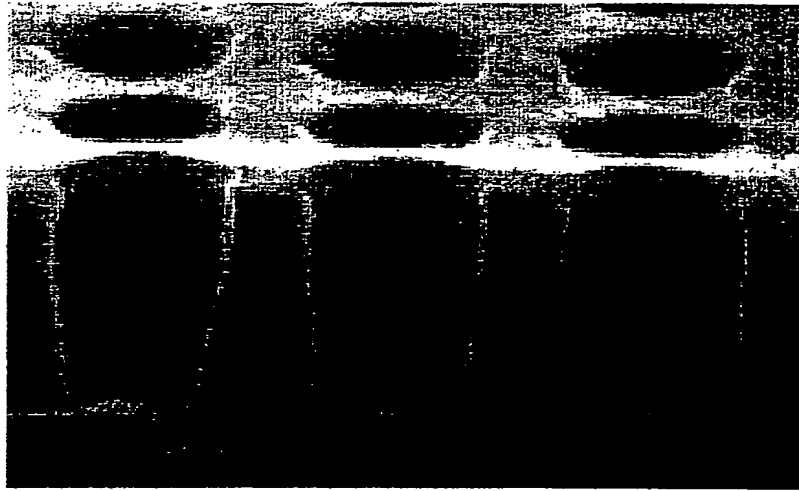


FIG. 2

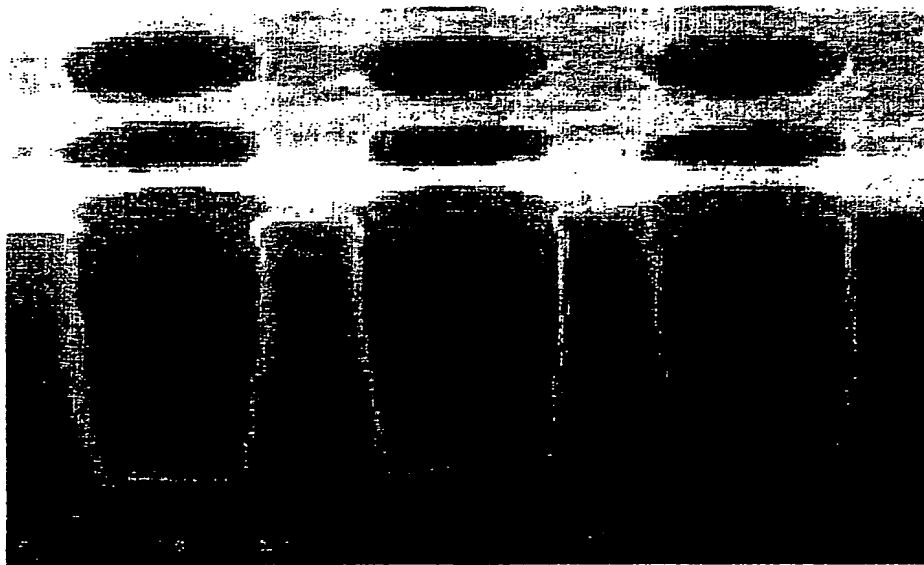


FIG. 3

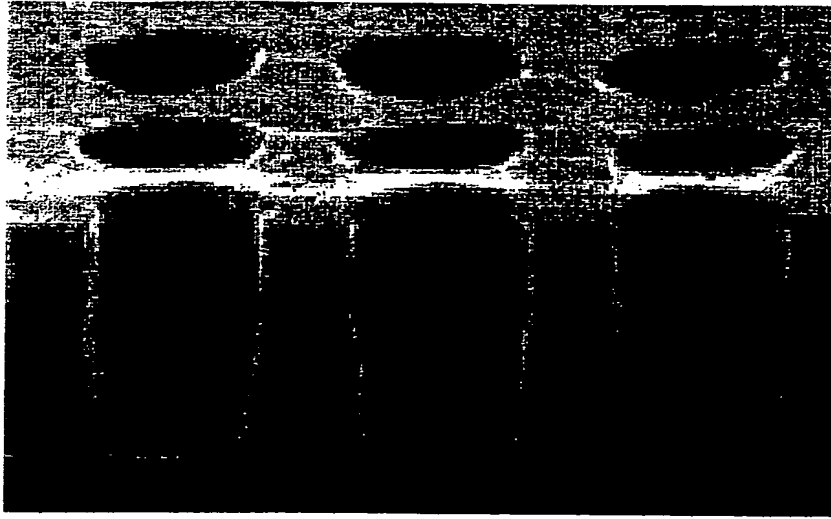


FIG. 4

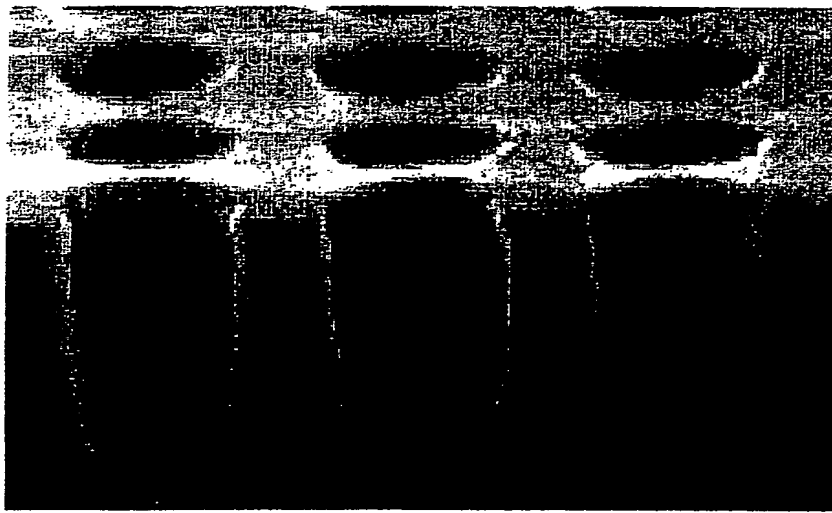


FIG. 5

**1. Abstract**

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**Abstract of the Disclosure**

Disclosed are compositions and methods for providing barrier layers for use in electronic device manufacture. Also disclosed are methods of reducing or eliminating poisoning of photoresists during electronic device manufacture.

**2. Representative Drawing**

Nothing

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